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THERMALLY MODULATED ELECTRON AFFINITY DETECTOR FOR PRIORITY POLLUTANT ANALYSIS

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16. ABSTRACT

In the area of environmental monitoring, a need exists for a rapid, sensitive, and selective method to analyze for chlorinated organic compounds such as pesticides, PCB, PCDD, and PCDF at trace levels in complex samples.

In response to this need, a program was conducted to determine the feasibility of using a new detector concept in the gas chromatographic analysis of certain priority pollutants. The concept is based on the thermal alteration of a compound's electron affinity in a flow-through reactor, which can be used to modify the selectivity and sensitivity of the ECD to certain compounds. The TM ECD consists of two ECDs connected by a temperature-controlled reactor. Different classes of organic compounds respond to the reactor conditions in different ways: some compounds exhibit an enhanced ECD response after passing through the reactor; others a diminished signal; and still others no change in the magnitude of the signal. The ratio of a compound's response from the post-reactor ECD to that obtained from the prereactor ECD appears to be a property characteristic of each compound. This peak area ratio can be used in conjunction with its retention time to increase the confidence level of the identity of a given compound while still taking advantage of the excellent sensitivity characteristics of the ECD.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report describes the development and evaluation of an analytical system designed to measure selected priority pollutants in various environmental media. The effects of varying catalyst and temperature to modify compound response for an electron capture detector were evaluated.

Robert L. Booth
Director
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ABSTRACT

In the area of environmental monitoring, a need exists for a rapid, sensitive, and selective method to analyze for chlorinated organic compounds such as pesticides, PCB, PCDD, and PCDF at trace levels in complex samples. Current methodologies typically employ analysis by GC-ECD, GC-HECD, or GC-MS for identification and quantification of the compounds of interest. Each of these approaches has its advantages and limitations.[1,2] The ECD usually provides the highest sensitivity for these types of analyses but this detector responds to any compound capable of capturing electrons in an ionized field including ubiquitous contaminants such as phthalate esters.[3,4] The HECD is very selective for chlorinated organic compounds when operated in the halogen-specific mode but it sometimes lacks the required sensitivity. Mass spectrometry provides unequivocal identification of compounds but also has problems with respect to adequate sensitivity and cost of analysis.

In response to this need, a program was conducted to determine the feasibility of using a new detector concept in the gas chromatographic analysis of certain priority pollutants. The concept is based on the thermal alteration of a compound's electron affinity in a flow-through reactor, which can be used to modify the selectivity and sensitivity of the ECD to certain compounds. The TM ECD consists of two ECDs connected by a temperature-controlled reactor. Different classes of organic compounds respond to the reactor conditions in different ways: some compounds exhibit an enhanced ECD response after passing through the reactor; others a diminished signal; and still others no change in the magnitude of the signal. The ratio of a compound's response from the post-reactor ECD to that obtained from the pre-reactor ECD appears to be a property characteristic of each compound. This peak area ratio can be used in conjunction with its retention time to increase the confidence level of the identity of a given compound while still taking advantage of the excellent sensitivity charcteristics of the ECD.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

C	-- centigrade
ECD	-- electron capture detector
GC-ECD	-- gas chromatography-electron capture detector
GC-HECD	-- gas chromatography-Hall electrolytic conductivity detector
GC-MS	-- gas chromatography-mass spectrometry
L	-- liter
Min.	-- minute
mL	-- milliliter
mm	-- millimeter
MS	-- mass spectrometry
ng	-- nanogram (10^{-9} gram)
PCB	-- polychlorinated biphenyl
PCDD	-- polychlorinated dibenzo-p-dioxins
PCDF	-- polychlorinated dibenzofurans
pg	-- picogram (10^{-12} gram)
TM ECD	-- thermally-modulated electron capture detector
µg	-- microgram (10^{-6} gram)
µL	-- microliter (10^{-6} liter)
US EPA	-- U.S. Environmental Protection Agency

SYMBOLS

Ar	-- argon
CH_4	-- methane

SECTION 1

INTRODUCTION

BACKGROUND

The potential for enhancing the selectivity and sensitivity of the ECD to certain compounds was demonstrated in preliminary studies conducted by R.C. Hall at Purdue University in 1973. These studies utilized a detector system comprised of two ECDs and a flow-through reactor. The detectors in this system were arranged in series, but were separated by a reaction chamber. A gold reaction tube and nitrogen carrier gas were used in this design.

It was found that at moderate reactor temperatures (up to 800°C), the response of the second detector was: reduced relative to the first for chlorinated hydrocarbon pesticides; approximately the same for PCBs; and greater for phthalate esters. At high reactor temperatures (950°C), PCBs and phthalates continued to produce a significant response in the second detector; most chlorinated hydrocarbon pesticides exhibited little or no response. The response ratio of the detectors was also found to be compound-specific and useful for confirmation of compound identity.

These phenomena were used to enhance detector selectivity by directly eliminating the response of certain components and by differentially summing the two detector signals to eliminate the response of stable components. These techniques were used to enhance detector selectivity to chlorinated hydrocarbon pesticides in the presence of PCBs and phthalates.

Although these preliminary results were encouraging, this approach was not studied in detail and did not cover a wide variety of compounds. The stability of the system was not verified and actual samples were not investigated. Consequently, funding was solicited to fully investigate the utility of the technique and determine the feasibility of constructing a commercial detector system based on this principle.

SCOPE OF WORK

The proposed program consisted of four phases. Phase I was designed to demonstrate the feasibility of the concept using existing off-the-shelf components. Phase II would involve the construction and evaluation of a breadboard detector. Construction and testing of a prototype detector would follow in Phase III. A detailed evaluation of the prototype detector would be conducted in Phase IV. Initial funding was sought and granted for only

the first phase, during which a number of specific objectives were required to be accomplished. They were:

- construction of a detection system;
- determination of response characteristics for selected compounds as a function of reactor temperature using at least two different materials as reactor tubes;
- investigation of response characteristics in different reaction gas compositions including nitrogen, argon/methane, and helium/hydrogen;
- determination of the most promising reaction tube/reaction gas combination;
- system evaluation with a limited number of model compounds;
- determination of the relation of detector response as a function of key operational parameters to reproducibility and signal stability for each compound studied;
- evaluation of detector specificity; and
- determination of an absolute detection level for each compound studied.

SECTION 2

CONCLUSIONS

In this initial phase of work, it has been demonstrated that a TM ECD system can have an enhanced selectivity for the determination of trace levels of chlorinated pesticides in environmental samples that have high levels of interferences. These interferences are compounds that exhibit an ECD response, specifically PCBs and phthalate esters, and are commonly present at significant levels in some environmental wastewater matrices. The output from a TM ECD can be differentially amplified to null the signals due to PCBs and phthalate esters and thereby isolate the signal due only to chlorinated pesticides. The development of the TM ECD could eliminate the necessity for sample extract cleanup in the screening by GC of environmental samples for the priority pollutant pesticides.

The optimum selectivity for chlorinated hydrocarbon pesticides was achieved when the TM ECD was operated with argon/methane reaction gas and a gold reaction tube maintained at 850°C. The TM ECD provides a response ratio which is generated by dividing the response in area units of ECD#2 by the response in area units of ECD#1. The magnitude of this ratio appears to be a function of chemical class. Phthalate esters exhibit a larger ECD response after passing through the reactor and yield a response ratio greater than one. Under the conditions listed above, PCBs display less than 10 percent reduction in response. As a result, their response ratio is approximately one. Chlorinated hydrocarbon pesticides exhibit a reduction in the post-reactor ECD response. Their resulting response ratios are therefore less than one. These TM ECD response characteristics provide the basis for the generation of a differential chromatogram in which chlorinated hydrocarbon pesticides are displayed as positive peaks, phthalate esters are presented as negative peaks, and positive PCB peaks are reduced by more than 90 percent.

SECTION 3

RECOMMENDATIONS

The evaluation of the detector prototype has demonstrated the validity of the TM ECD concept. A final determination of the detector's potential for widespread application in the area of environmental monitoring is not possible without additional work. The following areas merit continued investigation:

- determination of the reaction products responsible for the post-reactor signals;
- determination of molecular positional effects on the response factors of various isomers;
- utilization of capillary columns in conjunction with the TM ECD;
- definition of the limits of matrix effects on TM ECD response ratios; and
- optimization of TM ECD selectivity and sensitivity for PCDD and PCDF.

SECTION 4

EXPERIMENTAL

HARDWARE DEVELOPMENT AND PRELIMINARY EVALUATION

The chromatographic system used in this study consisted of a Radian 110B Gas Chromatograph modified to accept an experimental detector system which is shown schematically in Figure 1. It consists of two modified Tracor ECDs with a flow-through reactor between the two detectors.

The detectors were modified by replacing the 1/4-inch inlet fitting with a 1/16-inch fitting and reworking the top detector biscuit to reposition the exit port. The modification involved:

- removing the 1/4-inch inlet at the base of the detector and replacing it with a 1/16-inch bored-through male tube fitting;
- removing the 1/8-inch exit tube from the side of the top detector biscuit and plugging the resulting hole; and
- machining a female tube connection (10-32 thread with 39 degree ferrule seat) in the top face of the detector biscuit.

These modifications resulted in a straight flow-through carrier path of minimum volume. It also enabled the reaction tube and sample transfer inlet tube to be positioned flush to the detector cavity, thus eliminating stainless steel surfaces from the flow path.

The reactor used for this study consisted of a two-hole ceramic tube wrapped with resistance heating wire and enclosed in ceramic insultation. The reaction tube was inserted through one hole of the ceramic tube and a thermocouple in the other hole. Temperatures of the reactor were controlled $\pm$2°C from 350°C to 900°C.

A 1/8-inch o.d. glass-lined stainless steel column (1.8 mm i.d. x 168 cm long) was used for all separations. The exit of the column was interfaced to the first detector via a short piece of 1/16-inch o.d. (0.035-inch i.d.) gold tubing. Gold was used for this interface to prevent catalytic decomposition of the sample prior to detection.

All temperatures of the chromatographic system were controlled by the DART computer which is an integral part of the chromatograph. An inlet temperature of 226°C and detector temperatures of 340°C were used. The column temperature was varied to achieve the desired separation. Reactor

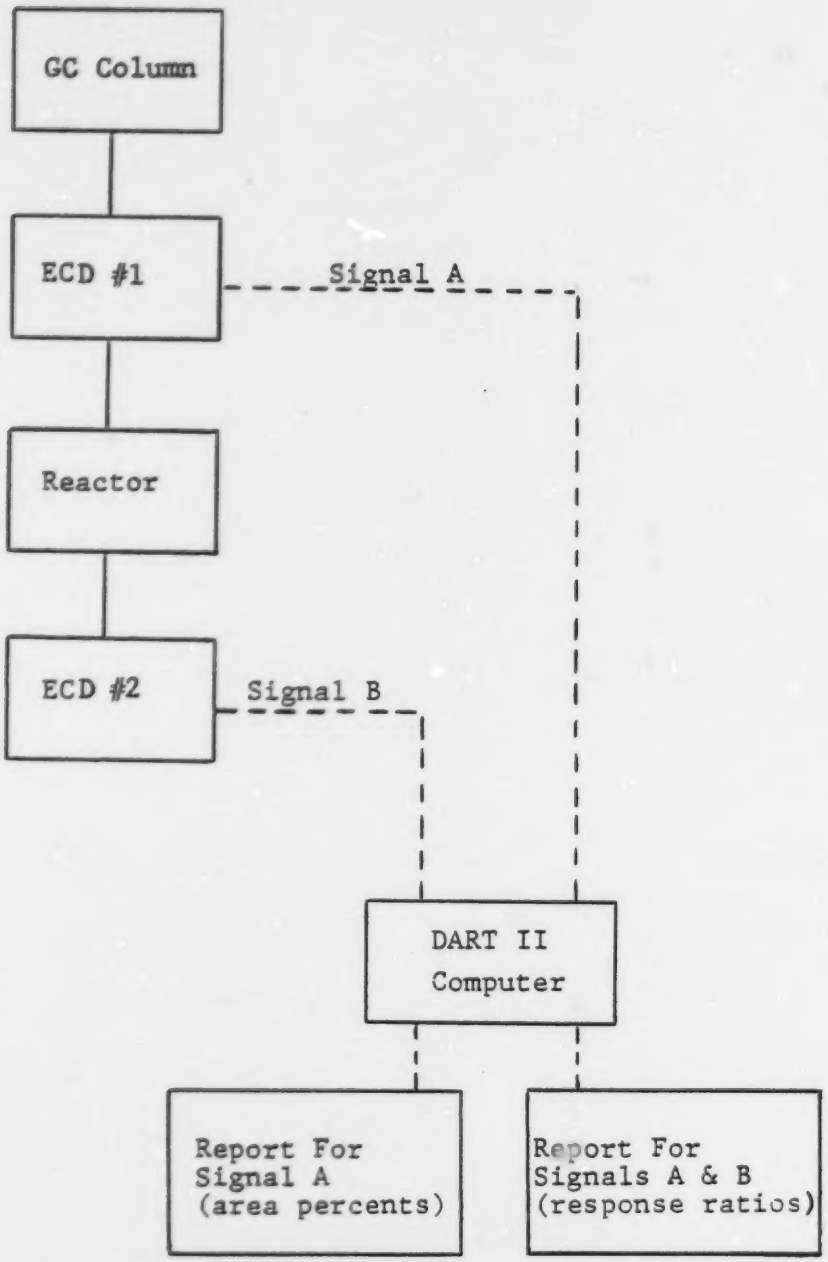

Figure 1. Block Diagram of Detector System

temperatures were varied from 350°C to 900°C. Detector outputs were routed through the DART II computer which integrated all peaks. The integration and chromatographic information were printed on a Teletype printer. A strip-chart recorder was also employed in order to obtain a record of the separation.

Seventeen model compounds were selected for use in the determination of the TM ECD's response characteristics. The basis for their selection was the fact that they represent electron-capturing analytes from a variety of compound classes including chlorinated hydrocarbon pesticides, PCBs, phthalate esters, organophosphate pesticides, chloroaromatics, nitroaromatics, and chlorophenols. The test compounds were grouped into mixtures each of which contained similar compounds that could be resolved chromatographically under the analytical conditions employed. The mixtures were introduced to the chromatograph in 5 µL injections. The total amount injected for each test compound and its absolute detection limit are presented in Table 1.

METHOD VALIDATION STUDY

The target compounds selected for use in the method validation study included phthalate esters and toxaphene. The validation study itself was based on the analytical procedures employed in US EPA's Method 608 for organochlorine pesticides and PCBs. The study was conducted based on the assumption that the phthalate esters were to act as interferants in the analysis of water samples for toxaphene.

The 200°C isothermal column temperature required for US EPA Method 608 precluded utilization of all six priority pollutant phthalate esters. At 200°C the 1.5% SP-2250/1.95% SP-2401 mixed phase column employed in the analysis of organochlorine pesticides would yield a chromatogram in which dimethyl phthalate and diethyl phthalate would be merged with the solvent front and di-n-octyl phthalate would elute well after the last toxaphene component. As a result, the following phthalate esters were selected for use in the method validation: di-n-butyl phthalate, benzyl butyl phthalate, and bis(2-ethylhexyl) phthalate.

System Linearity

Prior to initiating the method validation, the linear range of both the TM ECD and a commercially available linearized Ni^{63} ECD was established. This was accomplished by generating a five-point linearity check using toxaphene standards prepared at different concentration levels. Triplicate injections of each concentration level were made in order to ensure statistically valid data.

Preparation of Youden Pairs

The toxaphene spiking solutions used in the validation study were prepared as ten Youden pairs. Acetone was used as the solvent in order to enhance the water solubility of the concentrates. The spiking solutions were prepared at toxaphene levels that would yield sample concentrations ranging from 9.8 µg/L to 115 µg/L when 1.0 mL of the concentrate was used to fortify a 1 L water sample. The phthalate ester concentrations were prepared at a single level that would yield a sample concentration of 50 µg/L of each of

TABLE 1. COMPOUNDS USED FOR THE ELECTRON AFFINITY STUDY

	Compound	Amount (ng) Injected Into Chromatograph	Absolute Detection Limit (ng)
1.	Lindane	0.55	0.005
2.	Heptachlor	0.51	0.01
3.	Heptachlor Epoxide	0.48	0.01
4.	p,p'-DDE	0.50	0.03
5.	p,p'-DDT	0.50	0.05
6.	Aroclor 1254	5.20	0.3
7.	Aroclor 1016	5.03	0.1
8.	Toxaphene	5.00	0.1
9.	Chlordane	5.62	0.05
10.	Diethyl Phthalate	5.35	0.02
11.	Dibutyl Phthalate	5.40	0.02
12.	bis-(2-Ethylhexyl) Phthalate	5.25	0.02
13.	Methyl Parathion	0.52	0.01
14.	Ethyl Parathion	0.55	0.01
15.	1,2,4-Trichlorobenzene	0.50	0.007
16.	Nitrobenzene	5.00	0.1
17.	2,4-Dichlorophenol	5.00	0.1

the esters when a 1 L water sample was fortified with 1.0 mL of the concentrate. The toxaphene concentration in each of the spiking concentrates was verified by duplicate analysis against a toxaphene quality control check solution obtained from the Quality Assurance Branch of US EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio.

Phase I

The method validation study was conducted in three phases. During Phase I, twenty 1 L samples of reagent water were fortified with a 1.0 mL aliquot of spiking solution containing appropriate concentrations of toxaphene and the three selected phthalate esters. After spiking, the 20 water samples were extracted according to the protocol detailed in US EPA Method 608. Briefly, this involved extraction of the sample with three 60 mL portions of methylene chloride, drying of the combined extracts on an anhydrous sodium sulfate column, and concentration of the dried extracts followed by solvent exchange into hexane. A method blank was extracted with each set of samples using the protocol described above.

After extraction, the samples were analyzed on both a conventional ECD (ECD#1 in Figure 1) and TM ECD. The gas chromatographic parameters utilized in the method validation study are presented in Table 2. Quantitation of the samples was achieved by peak height comparisons against external standards.

Phase II

In Phase II, the extracts analyzed in Phase I were cleaned up on Florisil® columns using the procedure recommended in US EPA Method 608. The 6% diethyl ether in hexane eluate fraction was analyzed under the same chromatographic conditions as were used for Phase I. Prior to beginning this phase of the study, the Florisil® elution pattern for toxaphene was established using standard solutions.

Phase III

During Phase III, 1 L industrial wastewater samples known to contain toxaphene as a contaminant were extracted and analyzed according to US EPA Method 608 procedures. The analyses were conducted prior to and after Florisil® column cleanup using both detection systems.

A total of four toxaphene-containing wastewater samples were obtained for use in the validation study. One sample was divided into three 1 L aliquots.

Two of the aliquots were extracted and analyzed as previously described. The third aliquot was fortified with a toxaphene spiking solution as a method recovery check. The three remaining samples were each treated as single determinations.

TABLE 2. GAS CHROMATOGRAPHIC PARAMETERS FOR THE METHOD VALIDATION STUDY

Column -	168 cm X 1.8 mm i.d. glass-lined stainless steel packed with 1.5% SP 2250/1.95% SP 2401 on 100/120 mesh Supelcoport.
Temperature Program -	Isothermal at 200°C.
Carrier Gas -	5% methane/95% Argon at 35 mL/min.
Purge Gas -	5% methane/95% Argon at 25 mL/min.
Detector Temperature -	ECD - 340°C. TMEDC - 340°C.
Reactor Temperature -	850°C.
Inlet Temperature -	220°C.

SECTION 5

RESULTS AND DISCUSSION

Thermal stabilities of the 17 model compounds were determined with the detector configuration shown in Figure 1. The primary objective of this work was to find the most useful combination of temperature, carrier gas, and reaction tube material which can be used to differentiate between chlorinated pesticides, PCBs, phthalates, and chlorinated hydrocarbons.

RESPONSE RATIOS OBTAINED WITH ARGON/METHANE CARRIER AND A GOLD REACTION TUBE

The response ratios determined experimentally at various temperatures with argon/methane carrier and a gold reaction tube are presented in Table 3. The ratios shown are the average of three determinations. The standard deviations for the determinations are also shown. These ratios are based on the assumption that the response of ECD#1 and ECD#2 are equal for all compounds with an ambient reactor temperature. An ambient temperature for the reactor, however, was impossible to attain due to the temperature of the detectors (340°C each). Therefore, equal response was assumed and a reactor temperature of 350°C was used as the minimum temperature.

At 350°C, the response ratios were not equal to 1.0 for all compounds. This indicates that some rearrangement takes place either in the first detector or in the reaction tube at 350°C. The compounds altered the most were toxaphene, chlordane (both chlorinated hydrocarbons), and the phthalates.

As the temperature of the reactor was increased, the chlorinated pesticides were degraded to species less responsive to the electron capture detector. This resulted in response ratios less than 1.0. The response of ECD#1 and ECD#2 for the chlorinated pesticides at a reactor temperature of 900°C is shown in Figure 2. The most thermally stable chlorinated pesticides were p,p'-DDE and p,p'-DDT. Toxaphene and chlordane, both aliphatic chlorinated hydrocarbons, were found to be very unstable as shown by the data in Table 3 and the chromatograms reproduced in Figure 3.

PCBs, nitrobenzene, 1,2,4-trichlorobenzene and 2,4-dichlorophenol exhibited high thermal stability. The thermal stability of PCBs is well documented. Therefore, the response ratios were expected to be close to 1.0 and show little change as a function of temperature. The stability of nitrobenzene, 1,2,4-trichlorobenzene and 2,4-dichlorophenol was surprising. These compounds, particularly nitrobenzene and 2,4-dichlorophenol, are chemically reactive and were therefore expected to exhibit thermal instability.

TABLE 3. RESPONSE RATIOS[1] AT VARIOUS TEMPERATURES WITH Ar/CH_4 CARRIER AND A GOLD REACTION TUBE

Compound	Reactor Temperature (°C)					
	350	600	700	800	850	900
1. Lindane	0.93±0.01	0.93±0.01	0.90±0.01	0.11±0.01	0.05	0.04
2. Heptachlor	0.82±0.01	0.77±0.01	0.41±0.06	0.05	0.02	0.02
3. Heptachlor Epoxide	0.82±0.01	0.82±0.01	0.77±0.02	0.17±0.01	0.08±0.01	0.05
4. p,p'-DDE	0.81±0.01	0.83±0.01	0.82±0.01	0.59±0.02	0.48±0.01	0.40±0.01
5. p,p'-DDT	0.78±0.01	0.78±0.05	0.54±0.03	0.21±0.03	0.25±0.03	0.15±0.01
6. Aroclor 1016	0.98±0.02	1.00±0.01	0.98±0.02	0.92±0.03	0.92±0.01	0.85±0.01
7. Aroclor 1254	0.94±0.06	1.01±0.01	1.01±0.02	0.92±0.03	0.89±0.03	0.77±0.04
8. Toxaphene	0.61±0.06	0.64±0.02	0.05±0.03	<0.01	<0.01	<0.01
9. Chlordane	0.72 0.01	0.69±0.02	0.27±0.10	0.03	0.01	<0.01
10. Diethyl Phthalate	1.54±0.30	1.58±0.10	1.82±0.01	3.48±0.04	6.55±0.04	8.09±0.15
11. Dibutyl Phthalate	1.61±0.24	1.55±0.04	1.57±0.04	1.86±0.05	2.52±0.02	3.16±0.02
12. bis(2-Ethylhexyl) Phthalate	1.84±0.39	1.80±0.05	1.85±0.07	2.04±0.05	2.44±0.08	3.03±0.12
13. Methyl Parathion	0.90±0.01	0.89±0.01	0.31±0.01	0.09±0.01	0.08±0.01	0.07±0.01
14. Ethyl Parathion	0.92±0.01	0.91±0.01	0.26±0.01	0.09±0.01	0.09±0.01	0.08±0.01
15. Nitrobenzene	1.00±0.02	0.84±0.01	0.90±0.03	0.84±0.02	0.85±0.01	0.90±0.02
16. 1,2,4-Trichlorobenzene	0.82±0.01	1.02±0.02	0.97±0.01	0.92±0.01	0.93±0.01	0.91±0.01
17. 2,4-Dichlorophenol	1.07±0.03	1.04±0.01	0.90±0.05	0.85±0.03	0.75±0.01	0.77±0.03

[1]Based on equal response of ECD #1 and ECD #2.

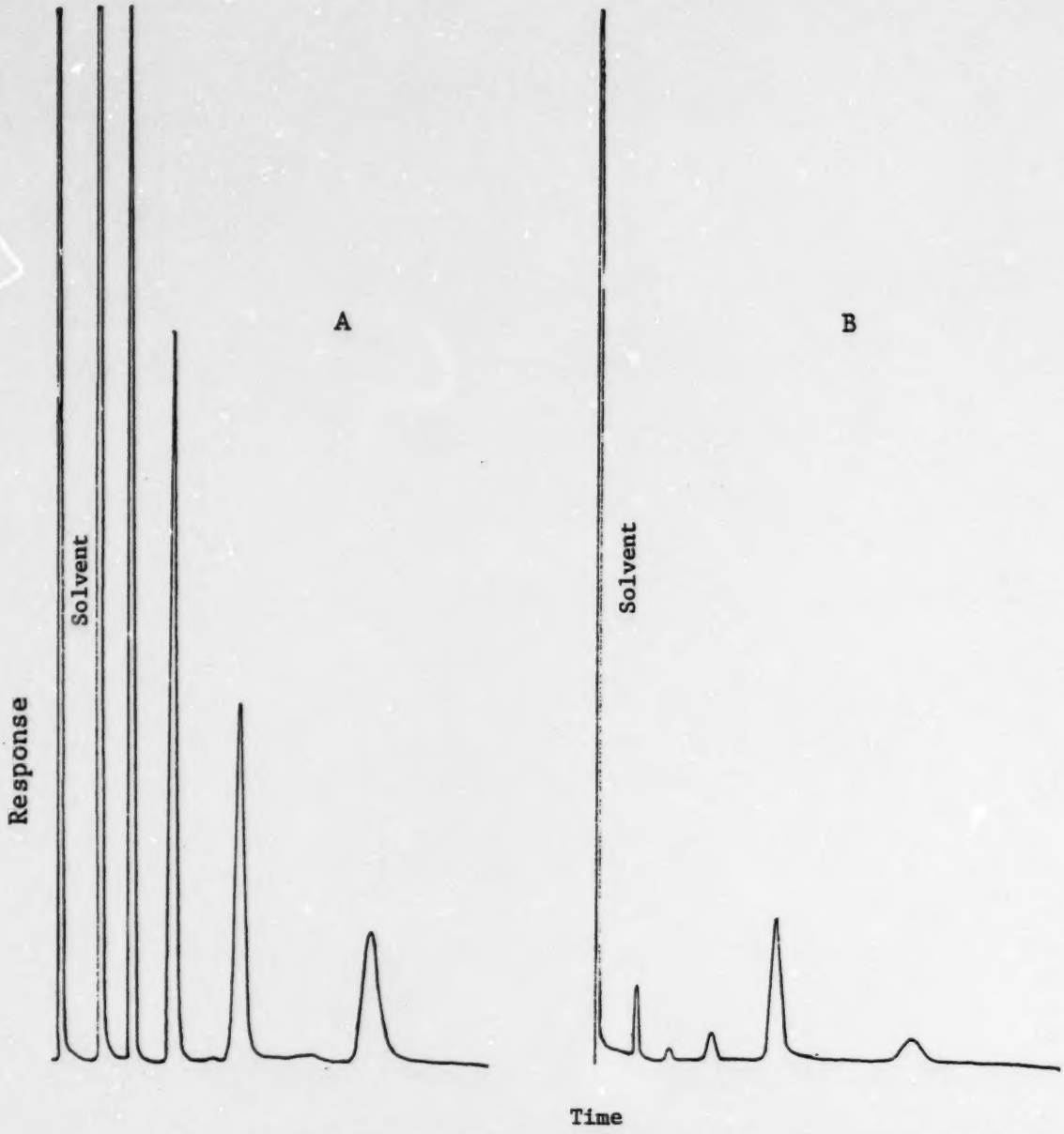

FIGURE 2. Chromatograms of Chlorinated Pesticides with Ar/CH_4 Carrier and Gold Reaction Tube

Order of elution: Lindane, Heptachlor, Heptachlor Epoxide, p,p'-DDE, p,p'-DDT

Chromatogram A, ECD #1, 500 pg of each component, X10 attenuation

Chromatogram B, ECD #2, 500 pg of each component after passing through a gold reactor at 900°C. Attentuation X10.

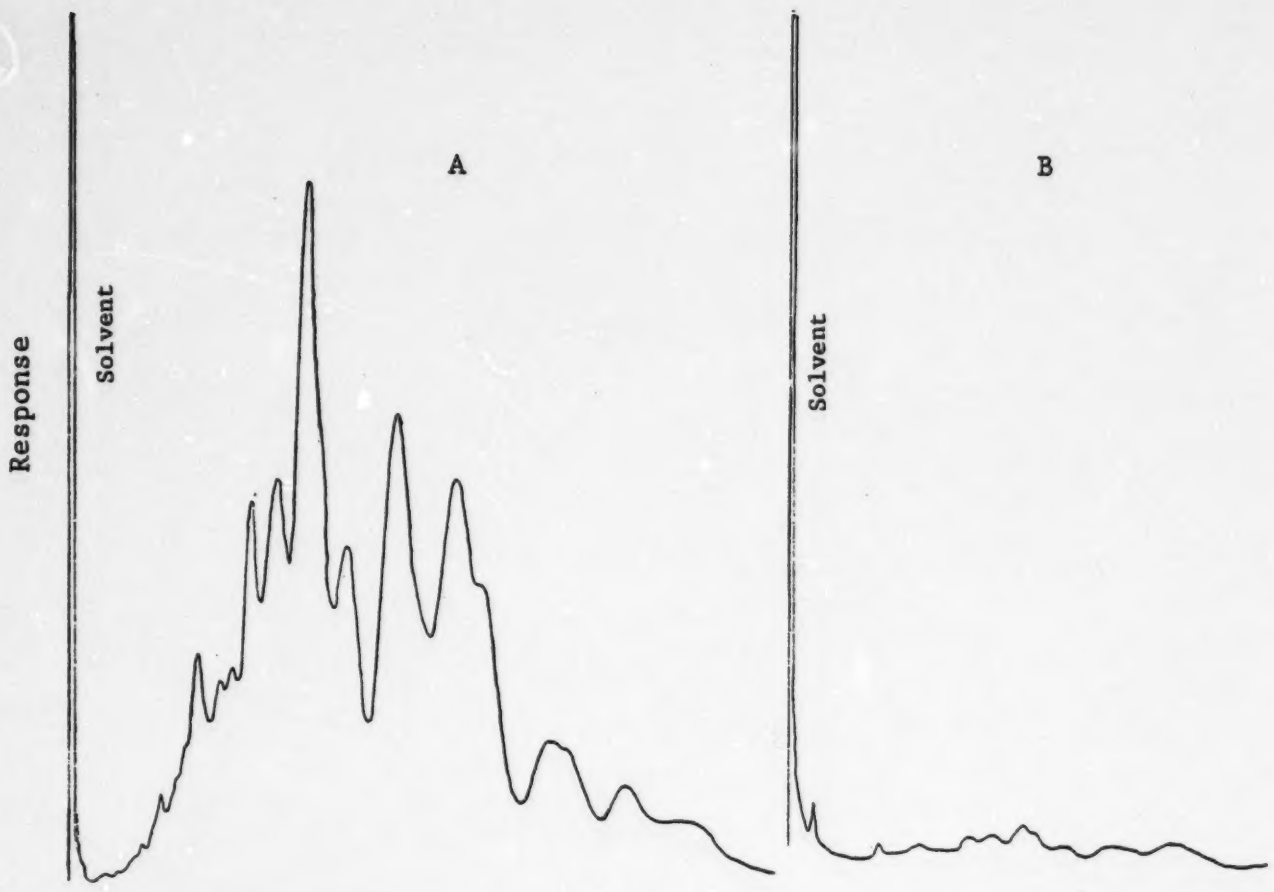

FIGURE 3. Chromatograms of Toxaphene with Ar/CH_4 Carrier and Gold Reaction Tube.

Chromatogram A, ECD #1, 5 ng of Toxaphene, Attenuation X5.

Chromatogram B, ECD #2, 5 ng of Toxaphene after passing through a gold reactor at 900°C, Attenuation X2.

Phthalates and the parathions were found to be thermally unstable. The organophosphate pesticides, methyl and ethyl parathion, were thermally degraded to products having very little electron affinity. As a result, the response ratios were quite small (see Figure 4). The phthalates were also very unstable. However, the products formed during the thermal degradation of the phthalates had a greater electron affinity than the parent compounds. Figure 5 illustrates the threefold enhancement of bis(2-ethylhexyl) phthalate and the eightfold enhancement of the diethyl phthalate at a reaction temperature of 900°C.

RESPONSE RATIOS OBTAINED WITH NITROGEN CARRIER AND A GOLD REACTION TUBE

The response ratios obtained at six reactor temperatures using nitrogen carrier and a gold reaction tube are shown in Table 4. In general, the results with nitrogen as the carrier were similar to those obtained with argon/methane. The chlorinated pesticides, the parathions, and the phthalates were again found to be thermally unstable. The PCBs, nitrobenzene, trichlorobenzene, and dichlorophenol, were found to be more thermally stable.

Chlorinated pesticides appear to be less stable with nitrogen carrier than with an argon/methane carrier. Significant degradation was observed at 700°C with nitrogen, whereas argon/methane required a temperature of 800°C before significant decomposition was observed. PCBs also appear less stable with a nitrogen carrier. For example, Aroclor 1254 has a response ratio of 0.77 at 900°C with argon/methane and a ratio of 0.29 at 900°C with nitrogen. This is illustrated by the chromatograms presented in Figure 6.

Comparison of the response ratios of phthalates with nitrogen and argon/methane carriers show contradictory results. The response ratio of diethyl phthalate is greater in nitrogen than argon/methane at 900°C (14.86 versus 8.09, respectively), but bis(2-ethylhexyl) phthalate has a greater response ratio at 900°C in argon/methane (3.03 versus 1.98 for nitrogen).

The remaining compounds, the parathions, nitrobenzene, 1,2,4-trichlorobenzene, and 2,4-dichlorophenol, displayed similar response ratios in nitrogen and argon/methane. It is interesting to note that the response ratio of nitrobenzene, gradually decreases as the temperature approaches 850°C, but then increase at a reactor temperature of 900°C for both nitrogen and argon/methane carriers.

RESPONSE RATIOS OBTAINED WITH HYDROGEN/HELIUM AND A GOLD REACTION TUBE

The response ratios for the helium/hydrogen gas composition were obtained by using a carrier of 30mL/min helium and a make-up gas of 30 mL/min hydrogen. The make-up gas was added to the column effluent immediately prior to entering the first detector.

Response ratios obtained with a helium/hydrogen carrier gas did not yield reproducible results as indicated by the data presented in Table 5. This table shows the response ratios obtained for the chlorinated pesticides at 350°C with different equilibration times. The phthalates also exhibited poor reproducibilities.

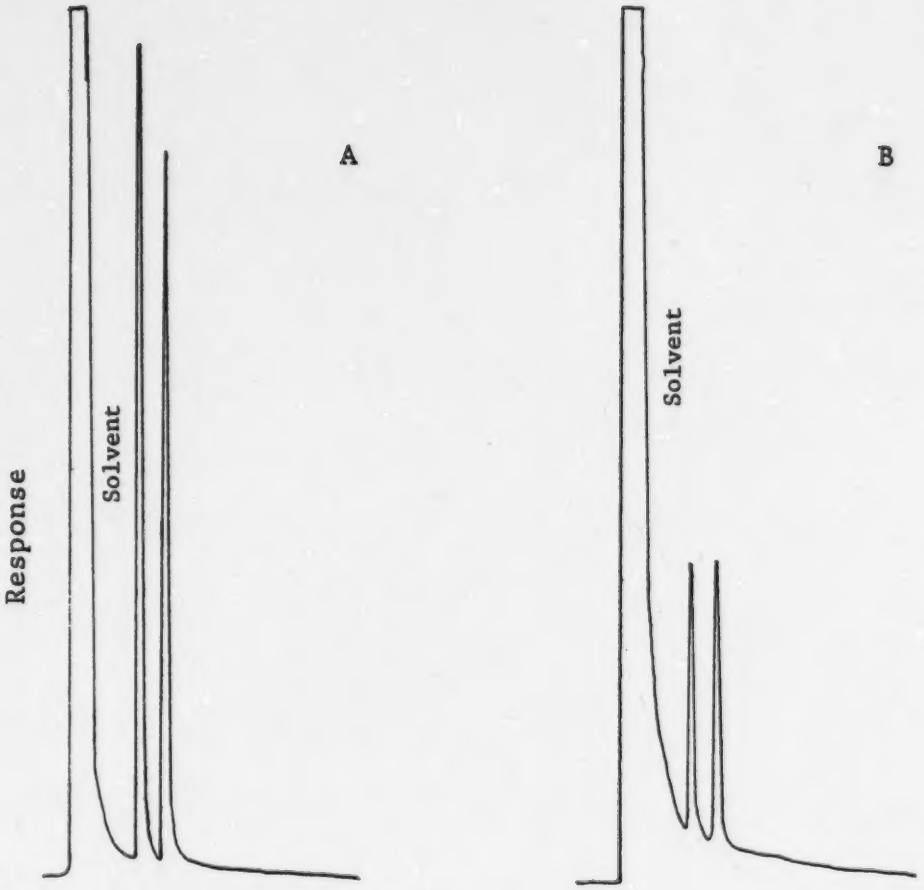

FIGURE 4. Chromatograms of Parathions with Ar/CH_4 Carrier and Gold Reaction Tube.

Order of elution: Methyl Parathion and Ethyl Parathion

Chromatogram A, ECD #1, 500 pg each, Attenuation X10.

Chromatogram B, ECD #2, 500 pg each after passing through a gold reactor at 900°C, Attenuation X2.

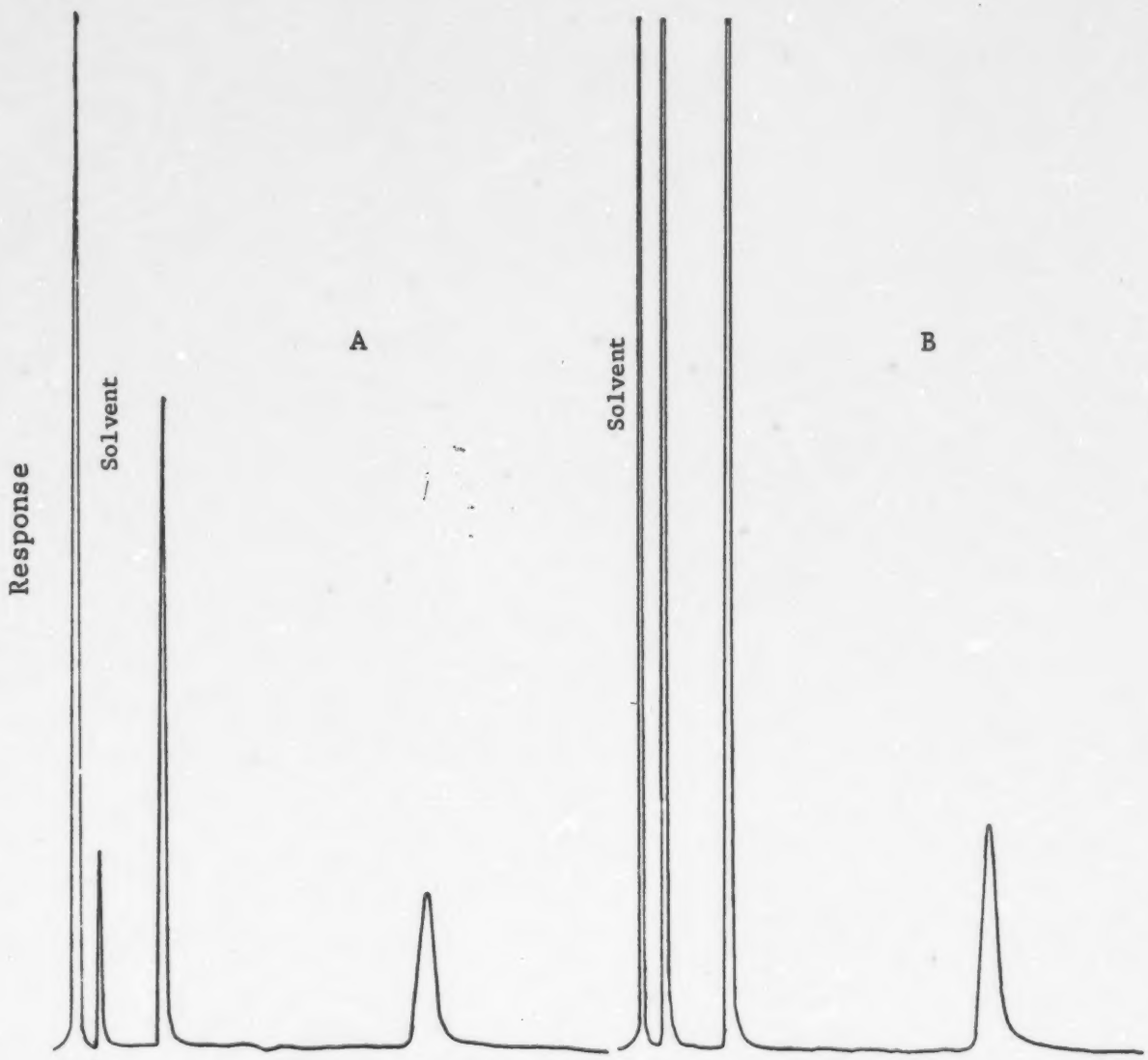

FIGURE 5. Chromatograms of Phthalates with Ar/CH_4 Carrier and Gold Reaction Tube.

Order of elution: Diethyl, Dibutyl, and bis(2-Ethylhexyl) Phthalate.

Chromatogram A, ECD #1, 5 ng of each, Attenuation X10.

Chromatogram B, ECD #2, 5 ng of each after passing through a gold reactor at 900°C, Attenuation X20.

TABLE 4. RESPONSE RATIOS[1] AT VARIOUS TEMPERATURES WITH NITROGEN CARRIER AND A GOLD REACTION TUBE

Compound	Reactor Temperature (°C)					
	350	600	700	800	850	900
1. Lindane	0.93±0.01	0.91±0.01	0.12±0.01	0.03	0.02	0.02
2. Heptachlor	0.47±0.03	0.38±0.01	0.04±	0.02	0.01	0.01
3. Heptachlor Epoxide	0.76±0.01	0.73±0.01	0.16±0.01	0.05	0.02	0.02
4. p,p'-DDE	0.75±0.01	0.73±0.01	0.49±0.01	0.17±0.01	0.10±0.01	0.09±0.01
5. p,p'-DDT	0.51±0.01	0.44±0.04	0.18±0.02	0.06±0.02	0.05±0.01	0.03
6. Aroclor 1016	0.97±0.01	0.95±0.01	0.83±0.01	0.72±0.02	0.63±0.01	0.60±0.01
7. Aroclor 1254	0.95±0.04	0.89±0.03	0.73±0.02	0.44±0.02	0.34±0.03	0.29±0.01
8. Toxaphene	0.61±0.01	0.51±0.02	0.09±0.01	0.04	0.02	0.02
9. Chlordane	0.73±0.01	0.71±0.01	0.03	0.01	<0.01	<0.01
10. Diethyl Phthalate	2.09±0.09	2.09±0.07	2.85±0.23	5.78±0.74	6.96±0.15	14.86±0.72
11. Dibutyl Phthalate	1.64±0.08	1.78±0.06	1.85±0.14	1.94±0.17	2.17±0.28	3.02±0.57
12. bis(2-Ethylhexyl) Phthalate	2.07±0.12	1.93±0.07	2.20±0.02	1.88±0.32	1.88±0.20	1.98±0.14
13. Methyl Parathion	0.86±0.01	0.68±0.02	0.17±0.01	0.10±0.01	0.07±0.01	0.07±0.01
14. Ethyl Parathion	0.88±0.01	0.60±0.02	0.18±0.01	0.12±0.01	0.09±0.01	0.08±0.01
15. Nitrobenzene	0.78±0.01	0.84±0.01	0.92±0.03	0.88±0.02	0.88±0.01	0.97±0.02
16. 1,2,4-Trichlorobenzene	0.98±0.01	0.99±0.01	0.98±0.02	0.92±0.03	0.90±0.01	0.90±0.01
17. 2,4-Dichlorophenol	1.04±0.04	0.98±0.03	0.69±0.03	0.57±0.03	0.60±0.02	0.72±0.02

[1]Based on equal response of ECD #1 and ECD #2.

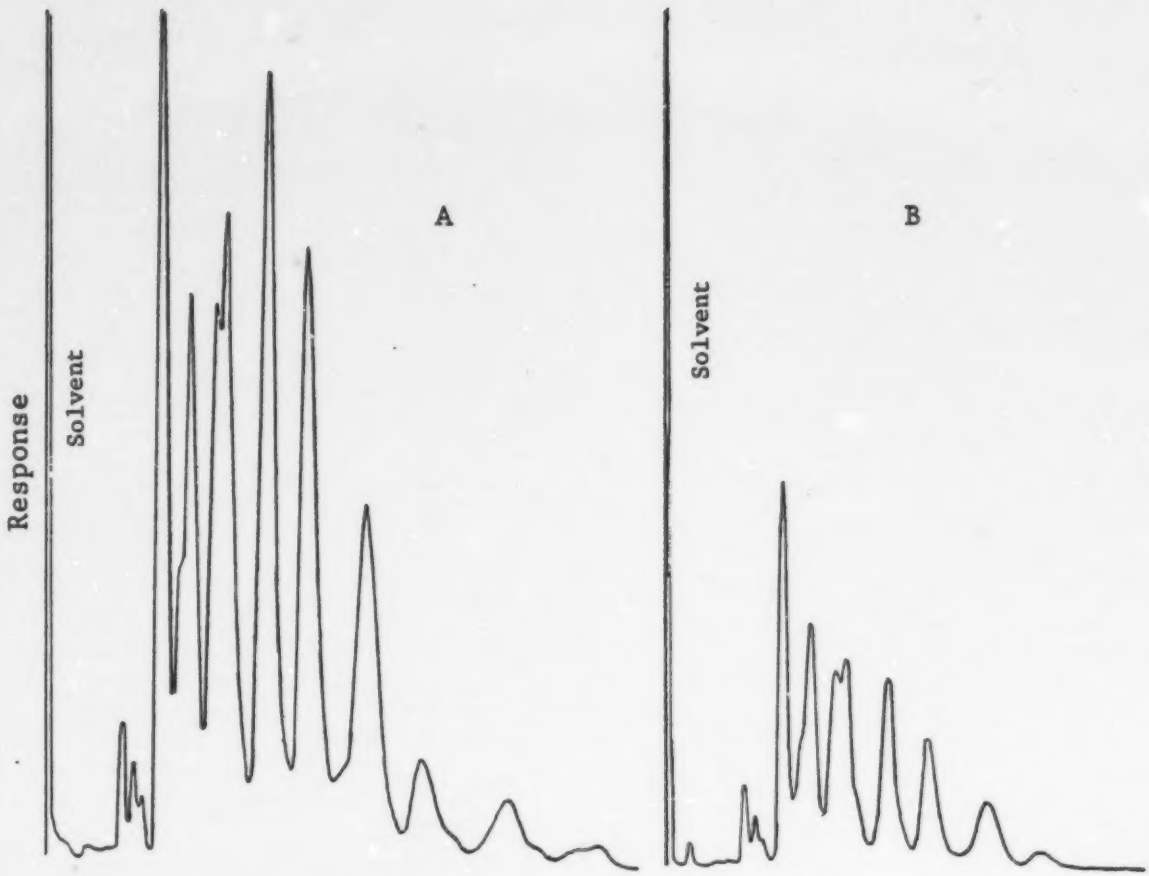

FIGURE 6. Chromatograms of Aroclor 1254 with Nitrogen Carrier and Gold Reaction Tube.

Chromatogram A, ECD #1, 5.2 ng of Aroclor 1254, Attenuation X10.

Chromatogram B, ECD #2, 5.2 ng of Aroclor 1254 after passing through a gold reactor at 900°C, Attenuation X10.

TABLE 5. RESPONSE RATIOS OF CHLORINATED PESTICIDES WITH HELIUM/ HYDROGEN CARRIER AND A GOLD REACTION TUBE AT 350°C

Compound	RESPONSE RATIOS (ECD #2/ECD #1) Held at 350°C for 1 Day	Held at 350°C for 2 Days	Reactor Heated to 900°C and Cooled to 350°C
Lindane	0.14	0.90	0.01
Heptachlor	0.30	0.43	0.08
Heptachlor Epoxide	0.39	0.88	0.09
p,p'-DDE	0.80	0.81	0.31
p,p'-DDT	0.23	0.45	0.07

Reproducible results were obtained for the PCBs, 2,4-dichlorophenol, and 1,2,4-trichlorobenzene. Toxaphene, chlordane, nitrobenzene and the parathions had very low response ratios at all temperatures, as indicated in Table 6, and were not studied in great detail.

Heating the reactor to temperatures above 800°C caused an apparent "activation" of the reaction tube. The reactor would require several days to return to its original level of activation once the temperature had been reduced. This "activation" caused very poor reproducibility, especially for the chlorinated pesticides and phthalates. The reactor "activation" was postulated to be due to a temperature dependent reaction between the hydrogen and some substance coating either the inside of the ECDs or the reaction tube. Removal of the material would then leave an active surface which could degrade compounds until a new "coating" was built up at lower temperatures by column bleed or reaction products. Regardless of the cause, this problem makes helium/hydrogen an unlikely choice for the carrier gas except for the thermally stable species.

Detector linearity with a helium/hydrogen gas composition was determined with the gold reaction tube at 600°C using standards spanning three orders of magnitude. The observed detector response was not linear over the complete range of concentrations. Similar results were obtained with dibutyl phthalate and p,p'-DDE. In addition, the response ratios determined were not consistent over three orders of magnitude for these compounds. The non-linear response observed is not surprising since the detector's relative pulse width was not adjusted for this gas composition.

RESPONSE RATIOS OBTAINED WITH HYDROGEN/HELIUM AND A NICKEL REACTION TUBE

Replacement of the gold reaction tube with a nickel tube did not alleviate the problems observed with gold. All compounds, except diethyl phthalate, were completely destroyed at a reactor temperature of 900°C. The "activation" of the reactor was again observed at high temperatures. After reducing the reactor temperature, several days were required for restoration of the original activity level.

The temperature at which the reaction tube was "activated" was determined to be approximately 860°C. Below 860°C, most of the compounds responded on ECD#2. Above 860°C, all of the analytes except nitrobenzene and diethyl phthalate were destroyed. The poor reproducibility and lack of discrimination in destroying the various compounds makes helium/hydrogen a poor gas composition for use with a nickel reaction tube.

RESPONSE RATIOS OBTAINED WITH NITROGEN CARRIER AND A NICKEL REACTION TUBE

Response ratios determined with a nitrogen carrier and a nickel reaction tube at six different temperatures are shown in Table 7. When compared to the results of both argon/methane and nitrogen with a gold reaction tube, the response ratios of the nickel tube with a nitrogen carrier were found to be lower at 350°C for every compound except the phthalates and nitrobenzene. The phthalates were observed earlier to have larger response ratios due to the formation of a degradation product with a greater electron affinity. The increased degradation of all compounds at 350°C with nitrogen/nickel suggested that catalytic reactions were occurring (i.e., the gold tube is more

TABLE 6. RESPONSE RATIOS OBTAINED WITH HELIUM/HYDROGEN CARRIER AND A GOLD REACTION TUBE AT FOUR TEMPERATURES

Compound	Temperature (°C)			
	350[1]	600	800	900
1. Lindane	0.14	<0.01	<0.01	0
2. Heptachlor	0.30	0.02	<0.01	0.02
3. Heptachlor Epoxide	0.39	0.02	0.01	0.01
4. p,p'-DDE	0.80	0.18	0.08	0.09
5. p,p'-DDT	0.23	0.09	0.07	0.07
6. Aroclor 1254	0.75	0.76	0.57	0.77
7. Aroclor 1016	0.76	0.75	0.76	0.77
8. Toxaphene	0.12	0.04	<0.01	0
9. Chlordane	0.33	0.02	<0.01	0
10. Diethyl Phthalate	3.76	7.08	12.86	20.29
11. Dibutyl Phthalate	2.01	2.74	2.84	3.93
12. bis(2-Ethylhexyl) Phthalate	2.26	2.05	2.18	2.36
13. Methyl Parathion	0	0	0	0
14. Ethyl Parathion	0	0	0	0
15. Nitrobenzene	0.08	0	0	0
16. 1,2,4-Trichlorobenzene	0.92	0.96	0.91	1.00
17. 2,4-Dichlorophenol	0.76	0.75	0.61	0.64

[1]Reactor held at 350°C for one day prior to analyses.

TABLE 7. RESPONSE RATIOS AT VARIOUS TEMPERATURES WITH A NITROGEN CARRIER AND NICKEL REACTION TUBE

Compound	Reactor Temperature (°C)					
	350	600	700	800	850	900
1. Lindane	0.85±0.01	0.84±0.01	0.66±0.05	0.35±0.04	0.03	0
2. Heptachlor	0.61±0.01	0.55±0.01	0.17±0.02	0.09±0.01	0.02	0
3. Heptachlor Exoxide	0.61±0.01	0.58±0.01	0.33±0.03	0.16±0.01	0.03	0
4. p,p'-DDE	0.54±0.01	0.53±0.01	0.45±0.01	0.36±0.01	0.17±0.01	0.02
5. p,p'-DDT	0.51±0.01	0.48±0.02	0.24±0.01	0.20±0.02	0.10±0.01	0
6. Aroclor 1016	0.73±0.01	0.74±0.01	0.71±0.01	0.63±0.01	0.05	0.01
7. Aroclor 1254	0.73±0.02	0.65±0.06	0.60±0.02	0.44±0.02	0.12±0.01	0.01
8. Toxaphene	0.47±0.02	0.47±0.02	0.35±0.02	0.12±0.04	0.01	0
9. Chlordane	0.63±0.01	0.59±0.01	0.49±0.01	0.18±0.02	0.01	0
10. Diethyl Phthalate	2.05±0.03	2.46±0.12	3.84±0.29	10.00±1.64	0.35±0.01	0.12±0.01
11. Dibutyl Phthalate	2.15±0.02	2.67±0.03	2.95±0.10	3.52±0.07	0.11±0.01	0.03
12. bis(2-Ethylhexyl) Phthalate	3.59±0.15	4.36±0.17	4.38±0.17	4.18±0.19	2.03±0.29	0.40±0.05
13. Methyl Parathion	0.72±0.01	0.69±0.01	0.57±0.03	0.02	0	0
14. Ethyl Parathion	0.74±0.01	0.69±0.01	0.45±0.01	<0.01	0	0
15. Nitrobenzene	1.49±0.02	1.49±0.02	1.31±0.01	0	0	0
16. 1,2,4-Trichlorobenzene	0.75±0.01	0.73±0.01	0.71±0.01	0.05±0.01	0.01	0
17. 2,4-Dichlorophenol	0.71±0.02	0.65±0.04	0.51±0.04	0.04	0.02	0.01

inert than the nickel tube). The nickel tube displayed another difference from the gold tube with nitrogen. At temperatures >800°C all compounds were degraded including the normally thermally stable PCBs, chloroaromatics and nitroaromatics. In addition, the response ratios of the phthalates were smaller suggesting that the intermediate species formed by the thermal degradation of the phthalates were degraded further to species which have small electron affinities. Due to these difficulties, this system was not investigated further.

RESPONSE RATIOS OBTAINED WITH ARGON/METHANE CARRIER AND A NICKEL REACTION TUBE

Response ratios obtained using an argon/methane carrier and a nickel reaction tube at six different temperatures are shown in Table 8. At 350°C, the response characteristics for the argon/methane carrier are very similar to those observed for a nitrogen carrier when a nickel tube is employed as the reactor. The reactivity of the nickel tube appears to increase more rapidly with a corresponding increase in temperature when argon/methane is used in place of nitrogen as the carrier.

This trend is evident when the values at a reaction temperature of 800°C are compared for the two systems. The response ratios of all the compounds except the phthalates are extremely small for the argon/methane system at 800°C whereas the response ratios of the chlorinated compounds and the phthalates resulting from the nitrogen system are significantly greater at the same temperature. The response ratios for the organophosphate pesticides, the chloroaromatics, and the nitroaromatics are very similar for both systems at this temperature.

In the case of the chlorinated pesticides, these data may be indicative of the occurrence of free radical formation in the argon/methane atmosphere within the nickel reactor followed by subsequent recombination reactions in which species are formed that have lower electron affinities. The nickel tube appears to act as a catalyst under these conditions since the test compounds exhibit much greater thermal stability when argon/methane is used in conjunction with a gold reaction tube. Because of these characteristics, this system was not selected for use in the validation study.

METHOD VALIDATION STUDY

System Linearity Check

In order to determine whether the prediction equation fits the five-point calibration data, measures of the adequacy of the fit were examined. In particular, residual plots were constructed and used as graphical aids in visually inspecting the fit of the prediction equation.

The plots of amount (ng) versus the response (mm) for both the commercial ECD and the TM ECD presented in Figures 7 and 8 respectively, indicate that a linear association between the two variables is the dominant relationship. Because of the minimum number of points, it is difficult to say whether other components, perhaps a quadratic term, should be added to the prediction equation.

TABLE 8. RESPONSE RATIOS AT VARIOUS TEMPERATURES WITH Ar/CH_4 CARRIER AND A NICKEL REACTION TUBE

Compound	Reactor Temperature °C					
	350	600	700	800	850	900
1. Lindane	0.84±0.01	0.82±0.01	0.73±0.01	0.01	0	0
2. Haptachlor	0.65±0.01	0.52±0.01	0.34±0.01	<0.01	0	0
3. Heptachlor Epoxide	0.62±0.01	0.59±0.01	0.48±0.01	0.01	0	0
4. p,p'-DDE	0.57±0.01	0.57±0.01	0.50±0.01	0.01	0.01	0
5. p,p'-DDT	0.53±0.02	0.46±0.02	0.37±0.01	0.03	0	0
6. Aroclor 1016	0.79±0.01	0.74±0.01	0.32±0.05	0.06±0.01	0.07±0.01	0.02
7. Aroclor 1254	0.85±0.02	0.67±0.08	0.43±0.10	0.04±0.01	0.05±0.01	0.01
8. Toxaphene	0.43±0.11	0.34±0.05	0.06±0.03	<0.01	0	0
9. Chlordane	0.66±0.02	0.49±0.01	0.25±0.02	0.04±0.02	0	0
10. Diethyl Phthalate	2.29±0.09	2.67±0.41	6.73±0.38	2.56±1.90	0.97±0.10	0.31±0.20
11. Dibutyl Phthalate	2.15±0.03	2.35±0.08	2.78±0.14	1.06±1.08	0.13±0.01	0.03
12. bis(2-Ethylhexyl) Phthalate	3.49±0.27	3.54±0.60	3.85±0.29	2.37±0.78	0.09±0.02	0
13. Methyl Parathion	0.80±0.01	0.48±0.04	0.08±0.01	0.02	0	0
14. Ethyl Parathion	0.85±0.01	0.51±0.03	0.11±0.02	0	0	0
15. Nitrobenzene	1.64±0.01	1.20±0.01	0.02	0	0	0
16. 1,2,4-Trichlorobenzene	0.79±0.01	0.76±0.01	0.46±0.03	0.14±0.02	0.12±0.02	0.07±0.01
17. 2,4-Dichlorophenol	0.79±0.04	0.74±0.01	0.06±0.01	0.06±0.02	0.05	0.02

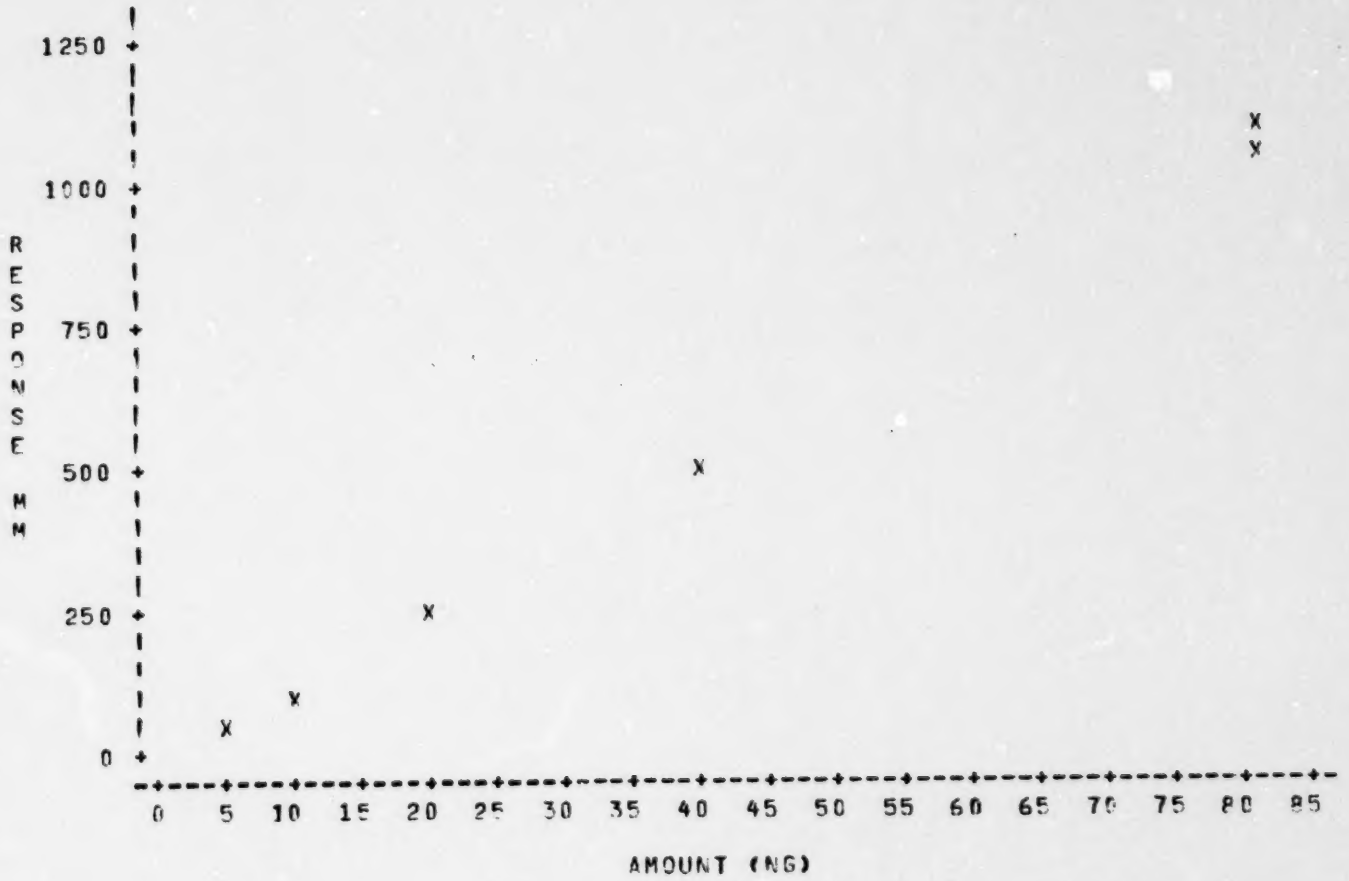

Figure 7. Linearity Plot - Commercial ECD

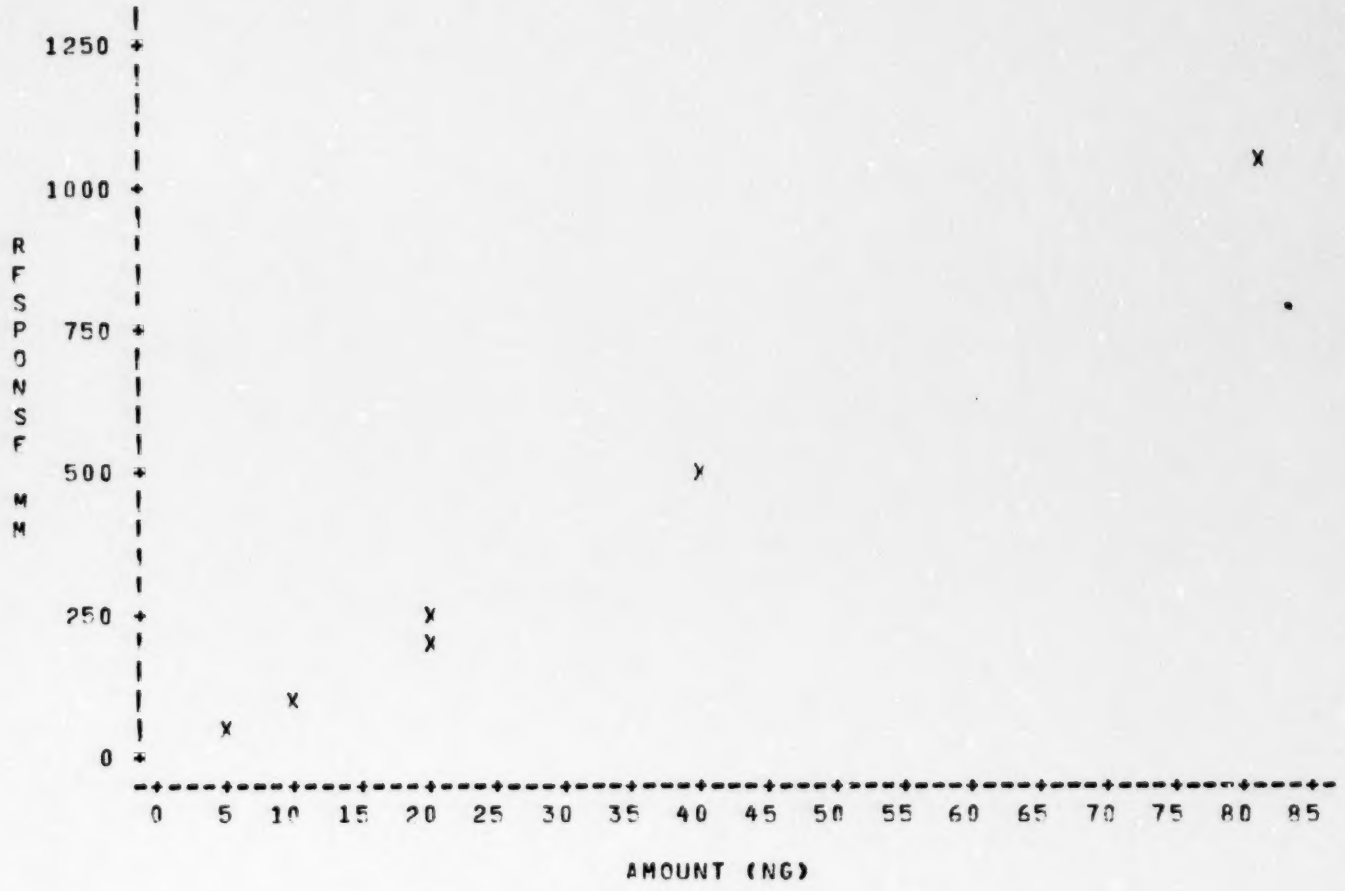

Figure 8. Linearity Plot - TM ECD

In investigating the possible need to include a quadratic term or some other component in the prediction equation, residuals of the linear fit were plotted against the amount (ng) for each of the two ECDs. The results did not indicate a need for some transformation of the predictor variable as the residuals appear to be randomly centered around the value zero.

As a further check on the adequacy of the linear fit, a quadratic term was assumed as part of the true underlying model:

$$\text{Response} = a + b_1 (\text{amount}) + b_2 (\text{amount})^2 + \varepsilon$$

where a, b_1, and b_2 are the unknown model parameters and ε is the error term.

The least-squares coefficient estimates exhibited below indicate that amount is the most influential determinant of the response for both detectors.

Detector	Intercept $\hat{a}$	Coefficient Estimates $\hat{b}_1$	$\hat{b}_2$
Commercial ECD	-27.5	12.8	0.01
TM ECD	-34.5	13.3	0.005

The hypothesis that $b_2 = 0$ was tested at 0.25 significance level (a very conservative test) with an individual t-test for each of the ECDs. Since the significance probabilities were greater than 0.25, the hypothesis of a zero regression coefficient (b_2) was not rejected.

It appears from the above analyses that the linear fit is appropriate for both the commercial ECD and the TM ECD. In addition, there does not appear to be a statistically significant difference in the linear response characteristics of the two detectors for toxaphene over the range of 5 ng to 80 ng.

Phases I and II

A phased approach was utilized in the method validation study in order to determine the effects of Florisil® column cleanup and sample matrix on the precision and accuracy of the analytical methodologies. The sample fortification and recovery data for Phase I of the method validation study are presented in Table 9. It should be noted that multiple data entries at a given concentration level are indicative of replicate analyses.

In addition, the data listed under the "ECD" category in Table 9 are the result of the chromatograms generated from the response of ECD#1 (Figure 1). The data tabulated under the "TMECD" heading were obtained from the chromatograms generated by the differential amplifier. This device subtracts the signal produced by ECD#2 from the signal generated by ECD#1. With this configuration, compounds with low response ratios (<1.0) yield positive peaks on the chromatogram while compounds with high response ratios (>1.0) produce

TABLE 9. METHOD VALIDATION STUDY: TOXAPHENE SPIKING AND RECOVERY DATA FOR PHASES I AND II

Youden Pair	True Value (µg/L)	Analyzed Concentration (µg/L)			
		Phase I (Pre-Cleanup)		Phase II (Post-Cleanup)	
		ECD	TMECD	ECD	TMECD
1	9.8	7.8, 7.9	7.8, 8.0	7.6	7.5
2	12.5	11.1	11.0	9.6	9.4
3	15.5	11.5	11.2	11.6	11.0
4	17.3	14.8	14.9	13.0	12.7
5	19.6	17.3	17.9	11.3	11.4
6	25.0	16.0	16.2	15.6	15.0
7	24.5	21.0	22.6	20.0	21.4
8	30.2	30.0	31.9	26.0	26.0
9	33.0	33.6, 33.0	31.7, 31.0	27.2	27.0
10	38.0	38.7	35.6	34.5	33.3
11	50.3	44.5	47.8	40.0	40.0
12	57.3	52.8	57.6	50.2	51.6
13	66.0	63.6	67.1	55.7	60.0
14	76.0	74.0	77.8	64.5	67.0
15	76.1	75.9	82.0	70.5	73.0
16	86.3	85.6	90.0	84.9	83.5
17	80.6	68.0	74.0	65.0, 65.0	76.0, 73.0
18	99.5	87.0	93.7	84.0	91.7
19	100.6	85.0	87.8	80.0	84.8
20	114.6	95.0, 100, 97.7	103, 106, 103	91.0, 91.9	98.0, 96.7

negative chromatographic peaks. Under the conditions used in this study, toxaphene produced positive peaks on the differential chromatogram while the phthalate esters exhibited a negative response.

For the recovery data presented in Table 9, the standard deviation appeared to depend on the toxaphene concentration, with constant proportion over all mean concentrations. Therefore, the percent relative standard deviation was judged to be the most useful measure of variation.

A statistical summary of percent recovery of toxaphene spiked in reagent water is presented in Table 10 for both the commercial ECD and the TMECD. The intralaboratory percent relative standard deviation (precision estimate) which indicates the repeatability of an individual laboratory or analyst when using the method is computed by:

$$RSD = \frac{S_r}{\text{mean percent recovery}} \times 100$$

where the single analyst standard deviation, S_r, was calculated from the Youden pair data and defined by Youden[6] as

$$S_r = \sqrt{\frac{\Sigma(D_i - \overline{D})^2}{2(n - 1)}}$$

where n = number of paired observations,

D_i = the difference in percent recovery between observations for a sample pair,

$\overline{D}$ = the average value for D_i.

A comparison of the two detectors in terms of accuracy and precision for both the pre- and post-cleanup methods can be made using the statistical summary given in Table 10. A graphical presentation of the accuracy and precision estimates are presented in Figures 9 and 10 respectively. It is apparent that the commercial ECD and the TM ECD work equally well for the analysis of toxaphene in fortified reagent water samples. This is true for both pre- and post-cleanup methods.

Additionally, it is observed that while the variability of recoveries using the post-cleanup method is significantly smaller than that for the pre-cleanup method, recoveries using the post-cleanup method are consistently lower.

Figures 11 through 14 graphically summarize the recoveries for the two types of detectors and cleanup methods used. The concentration level does not appear to affect the recovery of toxaphene.

A paired comparisons t-test was run to statistically test for differences between the two detectors and the pre- and post-cleanup recoveries. The results of this test were as follows:

TABLE 10. STATISTICAL SUMMARY: ACCURACY AND PRECISION ESTIMATES OF PERCENT RECOVERY FOR TOXAPHENE SPIKES IN REAGENT WATER

Method	Mean Percent Recovery[a]		% Relative Standard Deviation (RSD)[b]	
	Estimate	Approximate 95% Confidence Interval	Estimate	Approximate 95% Confidence Interval
Pre-cleanup				
Commercial ECD	89.1	(83, 95)	8.3	(5.7, 15)
TM ECD	92.2	(86, 98)	8.8	(6.1, 16)
Post-cleanup				
Commercial ECD	80.8	(79, 83)	3.0	(2.0, 5.4)
TM ECD	82.7	(80, 85)	3.5	(2.4, 6.4)

[a] $\text{Percent Recovery} = \frac{\text{Measured concentration}}{\text{True concentration}} \times 100$

[b] $\text{RSD} = \frac{S_r}{\text{Mean \% Recovery}} \times 100$ where S_r is the intralaboratory standard deviation (ppb)

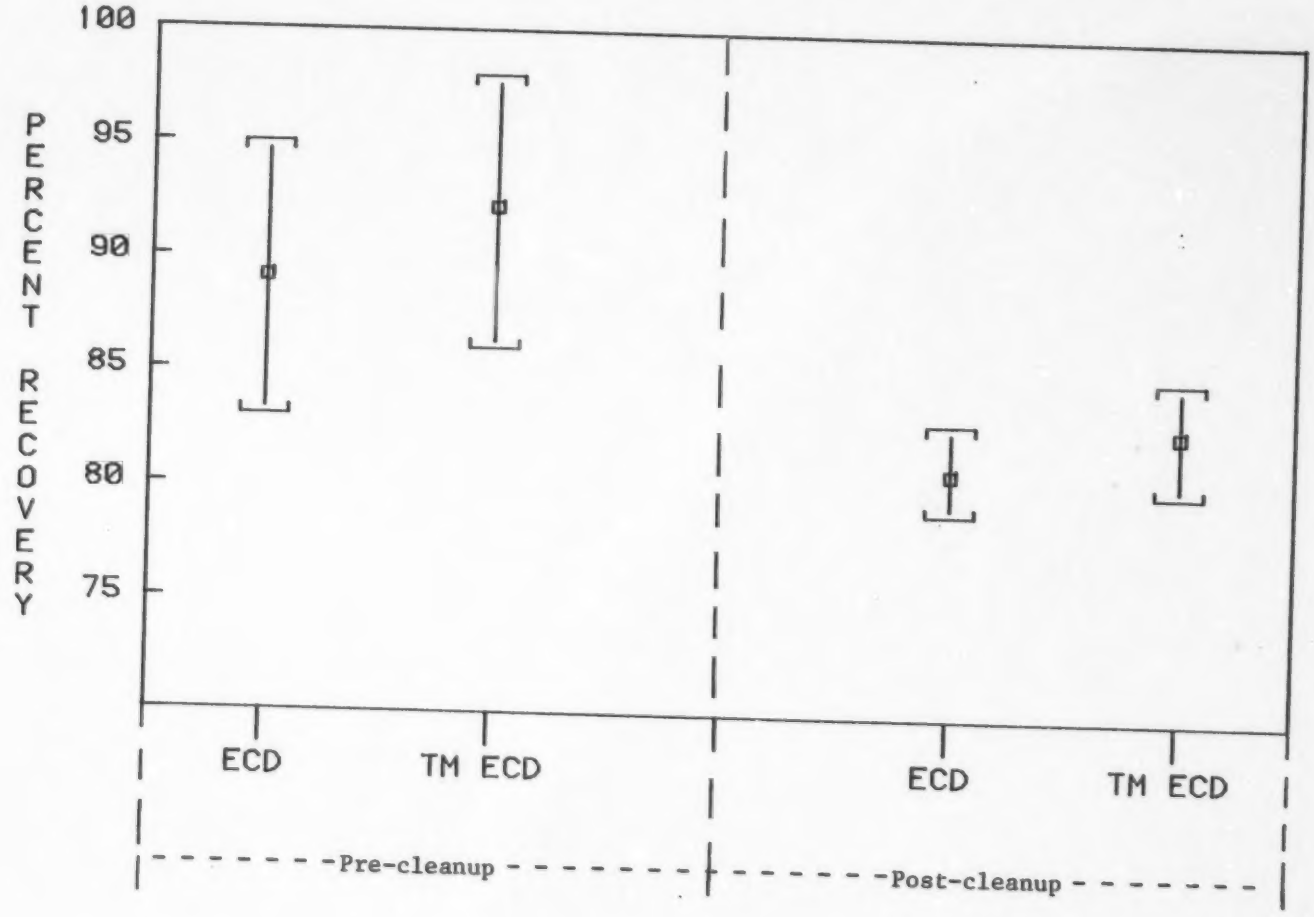

Figure 9. Accuracy Estimates: Phases I and II (Estimate ⊡ } 95% Confidence Interval)

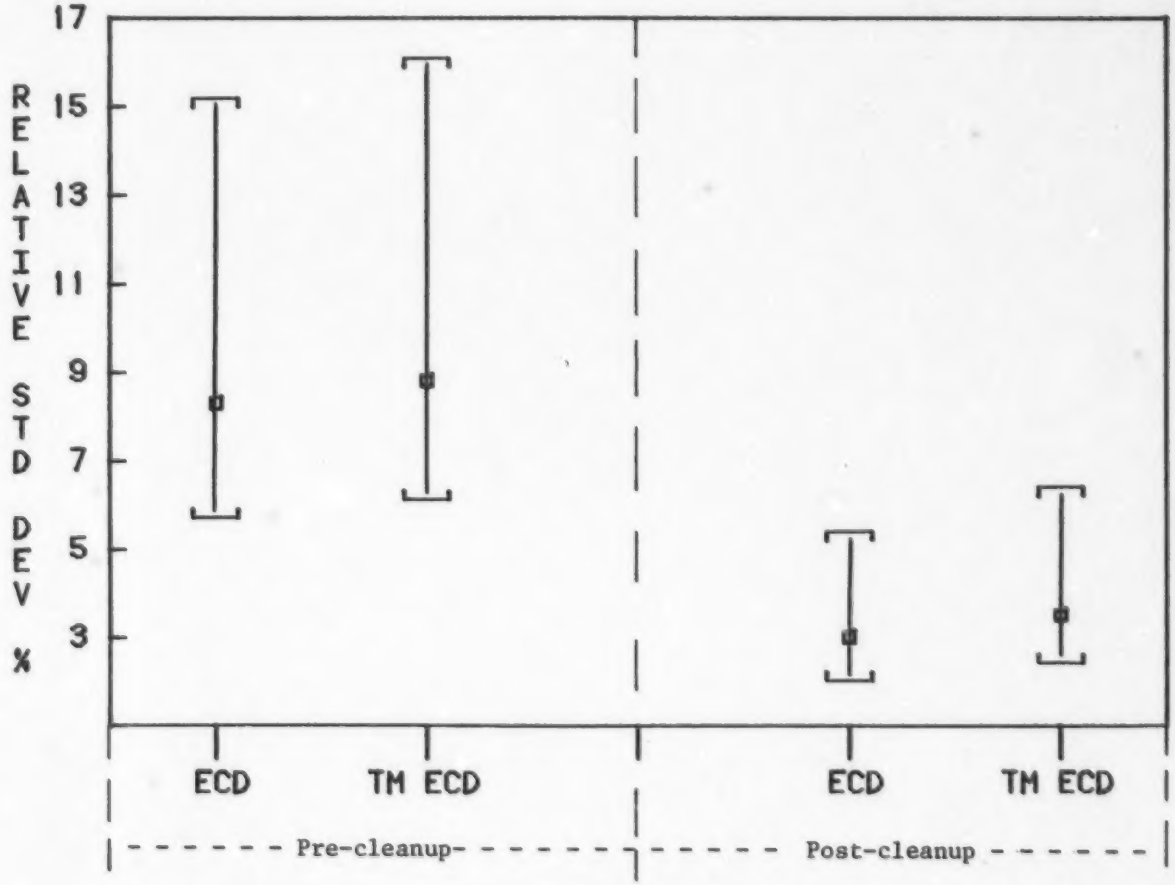

Figure 10. Precision Estimates: Phase I and II (Estimate ⊡ } 95% Confidence Interval)

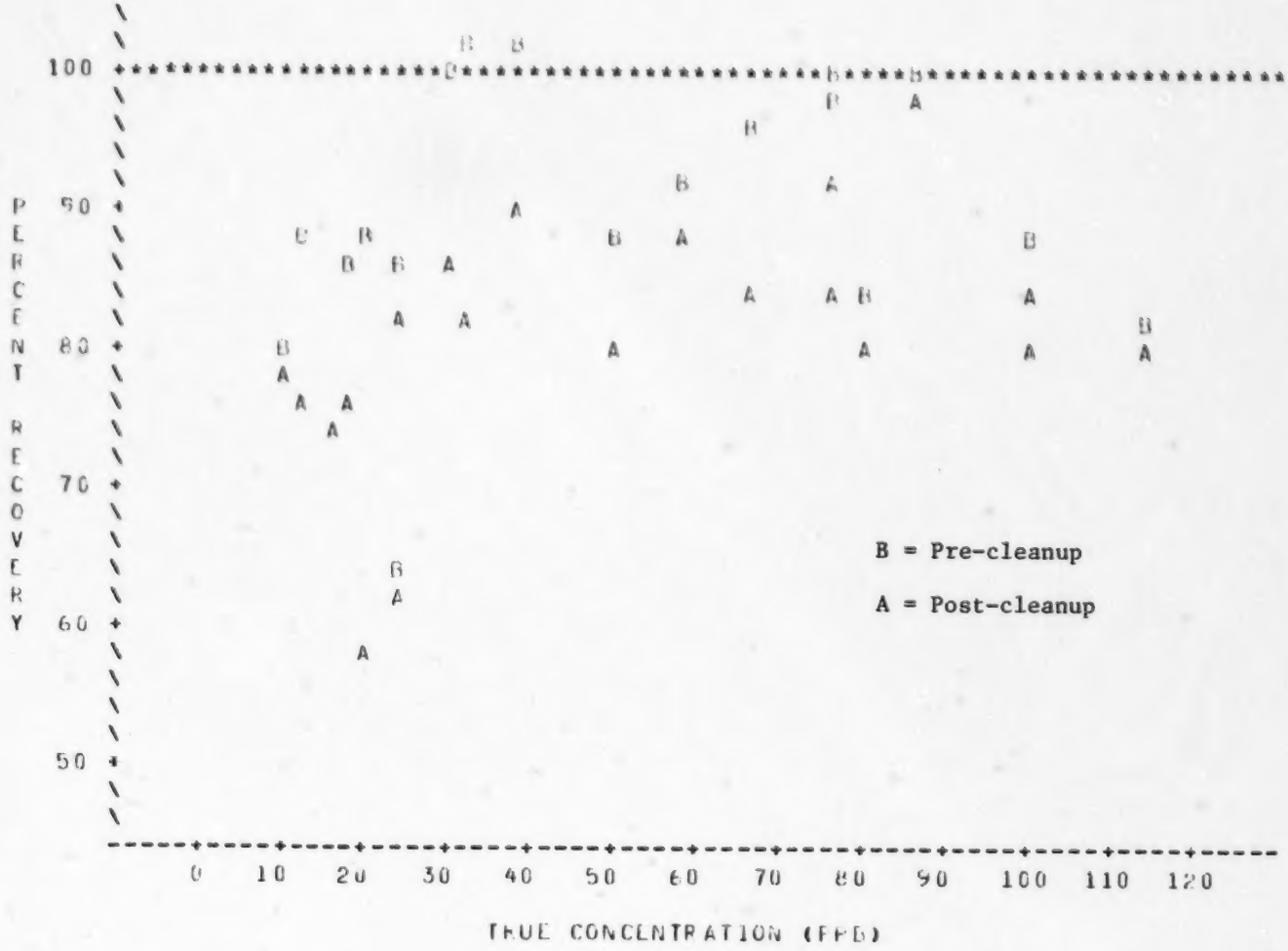

Figure 11. Percent Recovery Plot - Commercial ECD

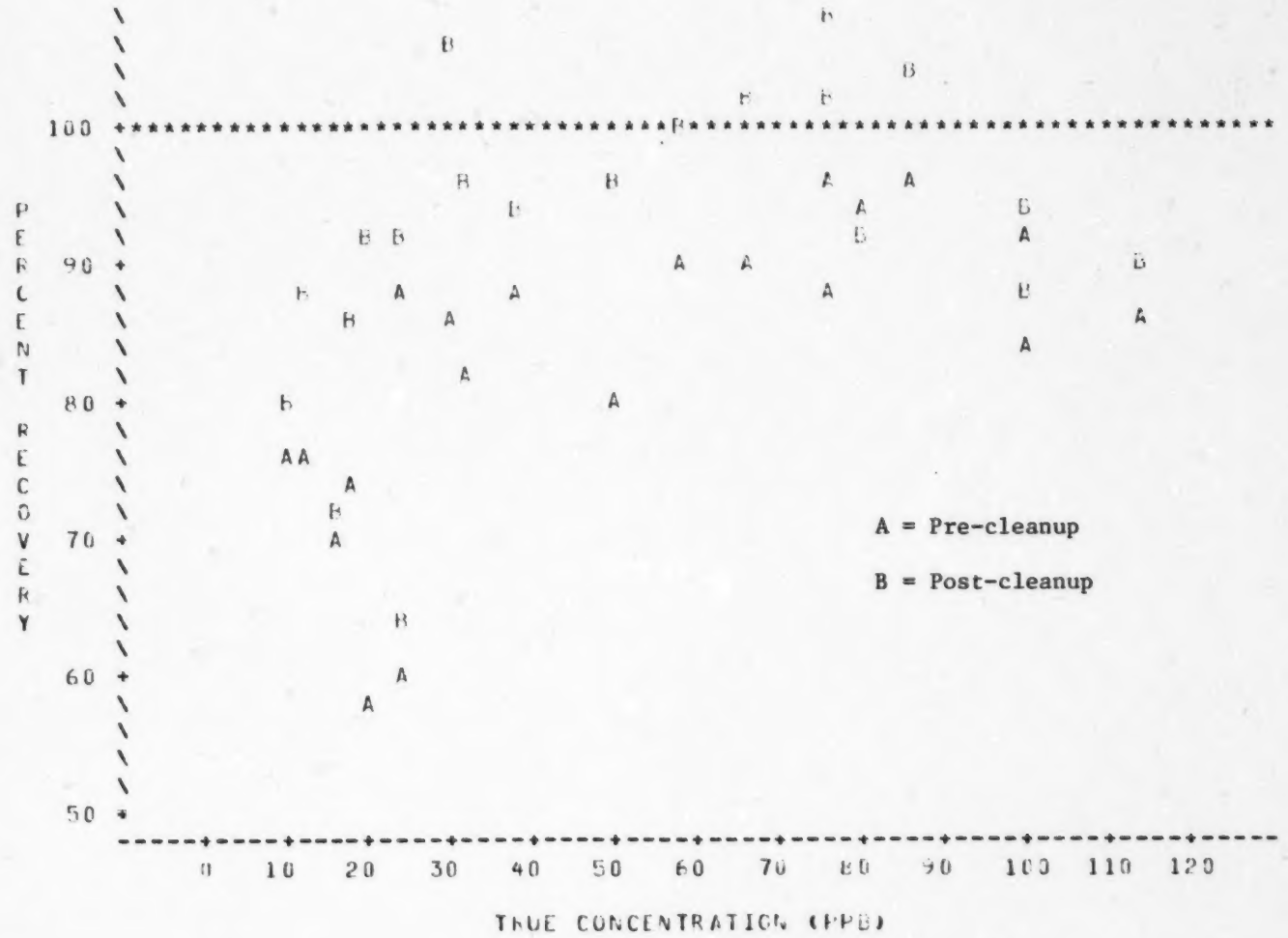

Figure 12. Percent Recovery Plot - TM ECD

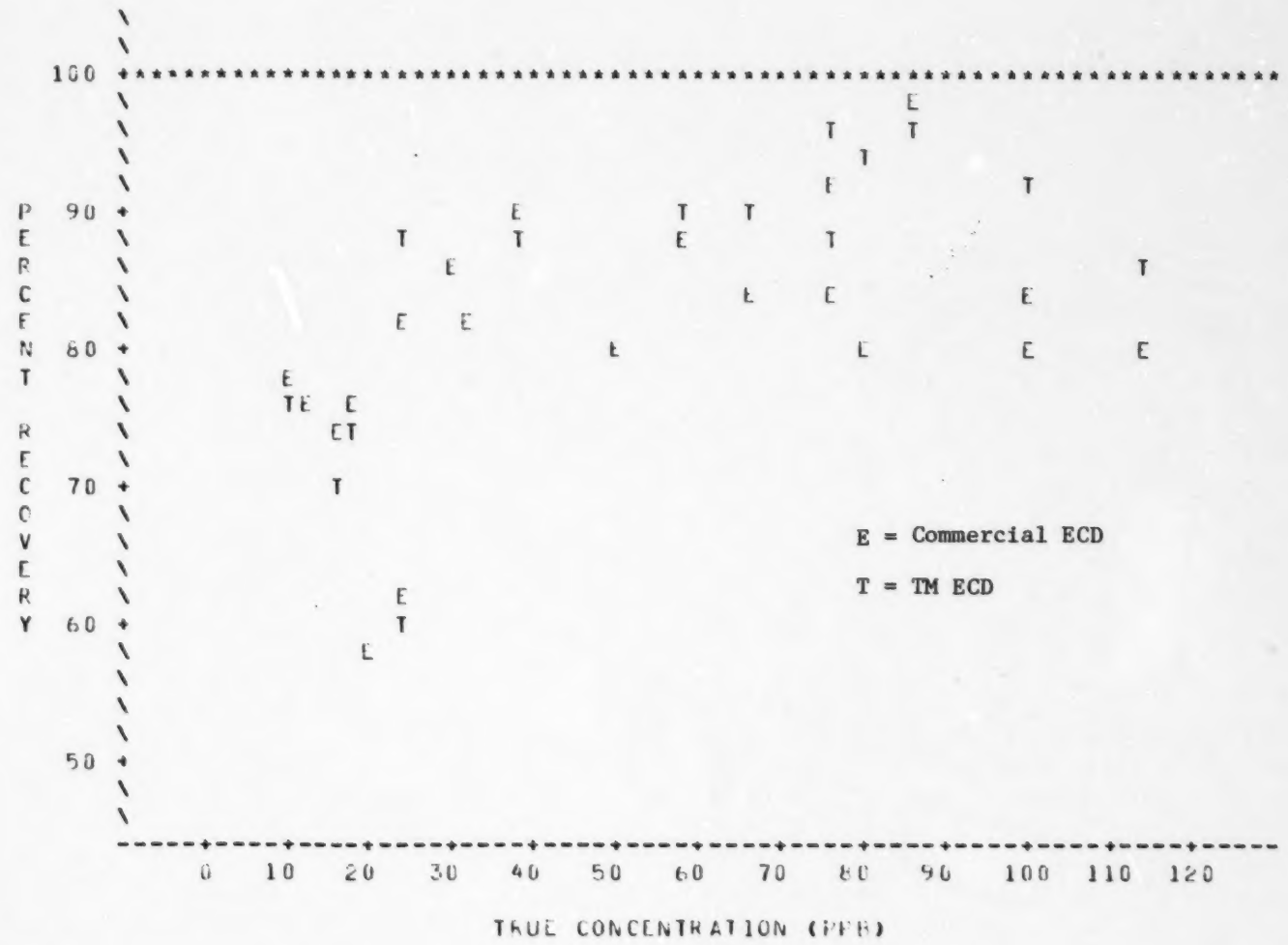

Figure 13. Percent Recovery Plot - Pre-Cleanup

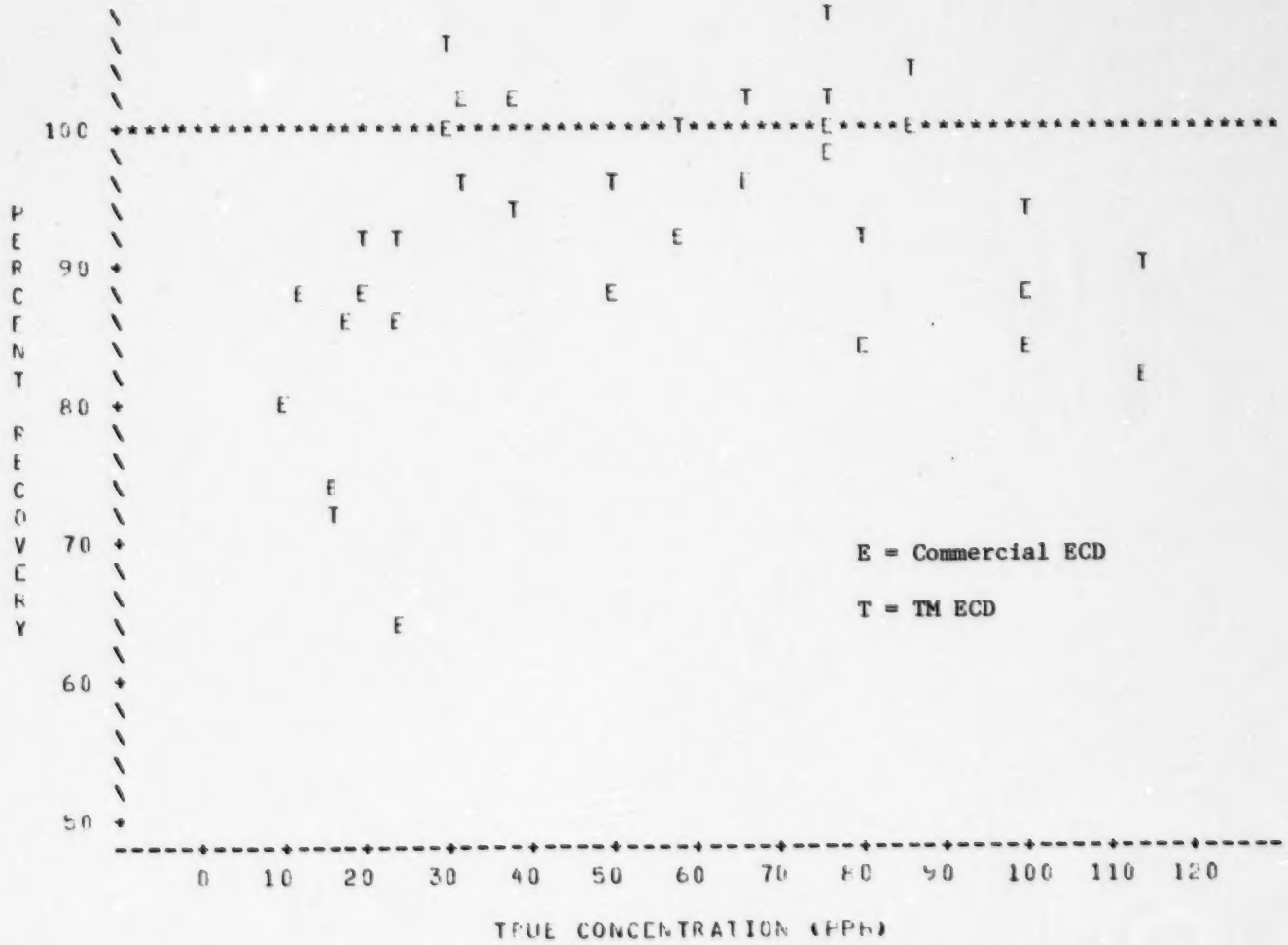

Figure 14. Percent Recovery Plot - Post-Cleanup

- The commercial ECD and the TM ECD are significantly different (at the 0.05 significance level) with respect to percent recovery for the precleanup method--TM ECD recoveries are closer to the true value; and

- The pre-cleanup and post-cleanup methods are significantly different (at the 0.05 significance level) with respect to percent recovery for both ECD detectors--pre-cleanup recovery results are closer to true value.

Phase III

The purpose of this phase of the method validation study was to determine the effect of sample matrix on the precision and accuracy of the analytical methodologies. Four industrial waste effluents known to contain toxaphene were analyzed using both detection systems prior to and after cleanup. One sample was of sufficient volume to be divided into three aliquots for a check on analytical precision. One of these aliquots was fortified with a toxaphene spiking solution at a level which would yield an equivalent sample concentration of 86.3 µg/L. The quantitation of the samples was achieved by peak height comparison against external standards. For all samples except X-2, a minimum of three peaks were used to quantitate the toxaphene concentration. The level of phthalate interference prior to cleanup was so great for sample X-2 that the quantitation was based on a single peak in the chromatogram. Figures 15 and 16 are illustrative of the differential chromatograms obtained for a sample containing only toxaphene and sample X-2 containing both toxaphene and phthalates respectively. The differential chromatogram of sample X-2 after cleanup is presented in Figure 17. It should be noted that the same peaks were used in the quantitation of the toxaphene concentrations for both detection systems. The analytical data for the industrial waste samples are summarized in Table 11.

A statistical summary of recovery precision for toxaphene in effluent samples is given in Table 12 for the two detectors. As was illustrated for clean samples, the TM ECD appears to be equivalent to the commercial ECD in this particular application. Figure 18 is a graphical presentation of the precision estimates for toxaphene in waste effluents. The method detection limit for this type of sample is estimated to be 5 µg/L. The results of the method recovery check listed in Table 13 indicate quantitative recovery of toxaphene from the fortified industrial waste sample.

Phthalic Anhydride Experiment

An additional series of analyses using the TM ECD were performed in an attempt to identify the mechanism responsible for the enhanced phthalate response. It was hypothesized that phthalate esters were being converted to phthalic anhydride within the heated reactor and that the enhanced signal was the result of the relatively greater electron affinity of the anhydride. To test this hypothesis, a 5 ng/µL phthalic anhydride in acetone solution was analyzed on the 110 GC equipped with the TM ECD. The analysis was performed at two different reactor temperatures: 650°C and 850°C. The response ratio for this compound was calculated and found to be 0.87 for both reactor temperatures. This indicates that the phthalic anhydride is thermally stable under the conditions employed. These conditions included a gold reactor tube

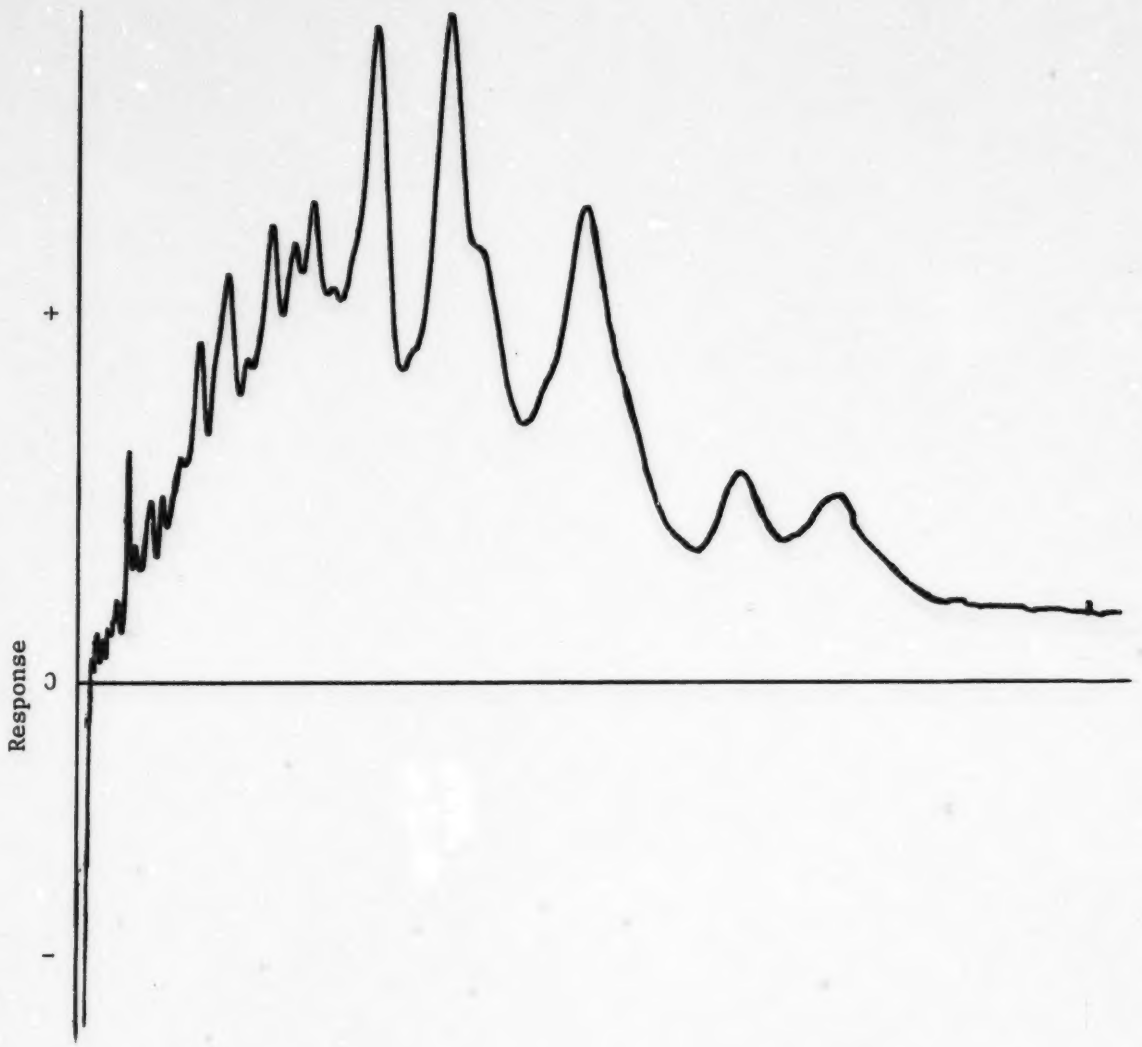

Figure 15. Differential Chromatogram of a Toxaphene-Contaminated Industrial Waste (128 µg/L)

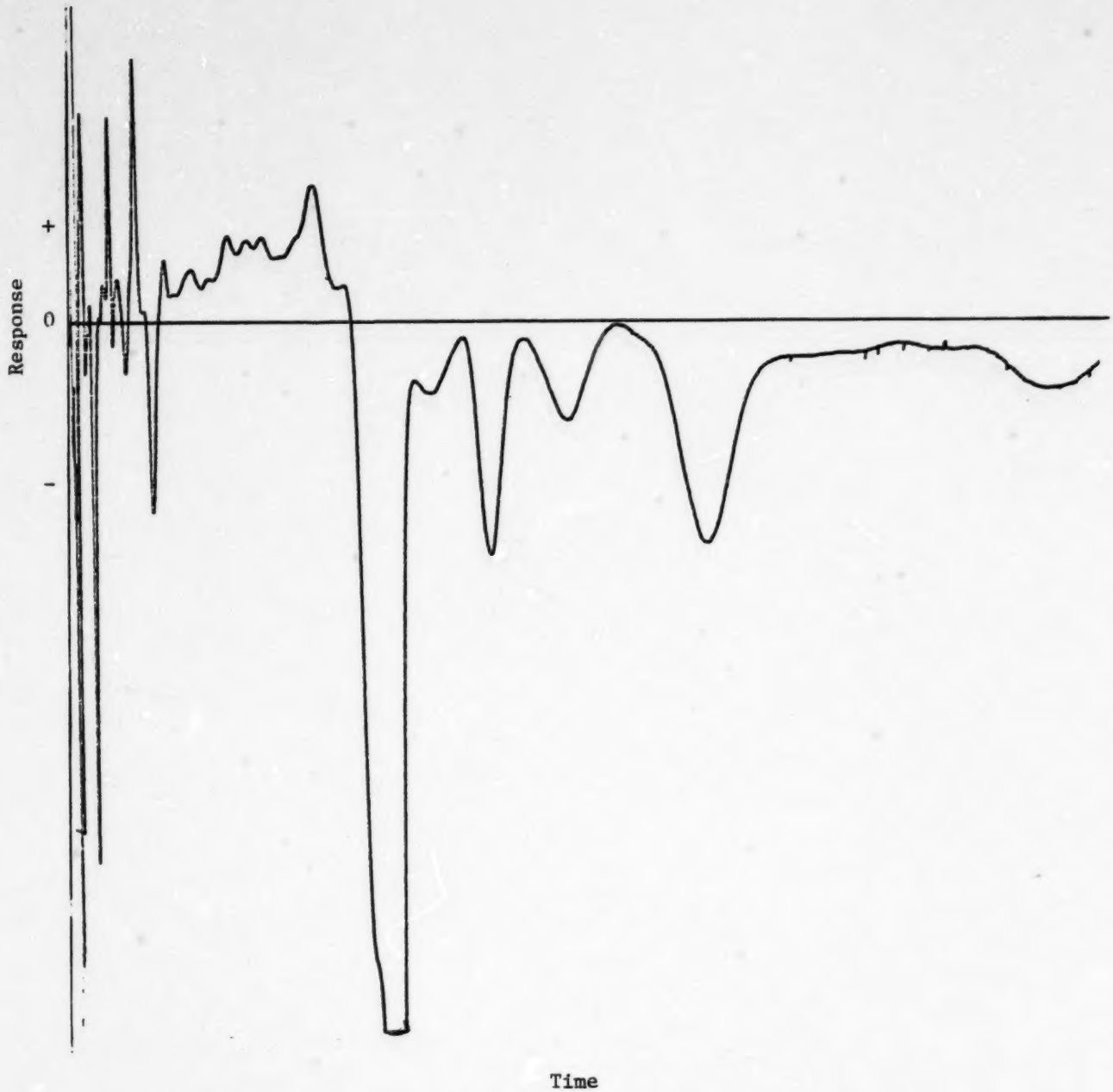

Figure 16. Differential Chromatogram of Sample X-2 Prior to Cleanup (43.2 µg/L)

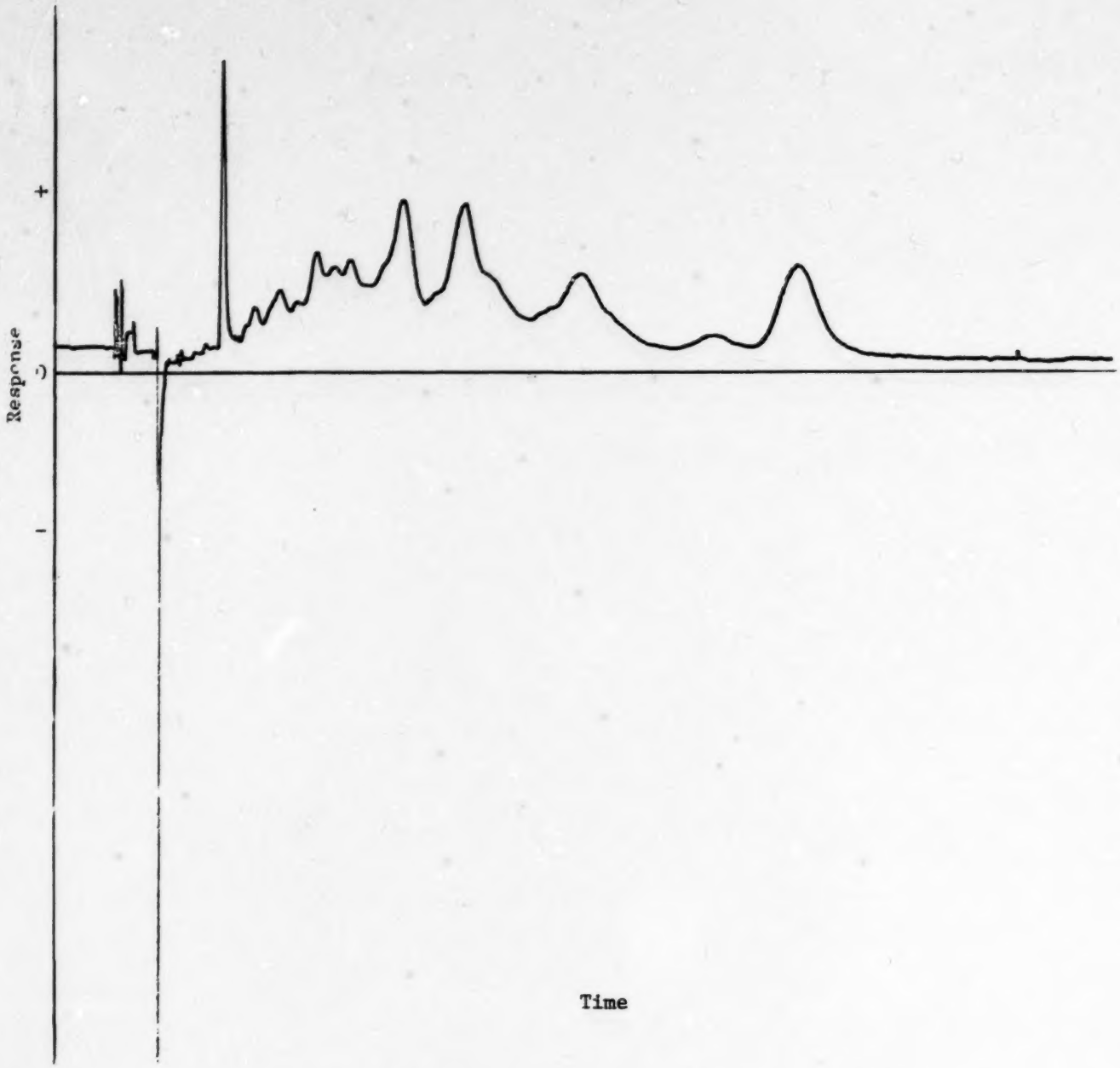

Figure 17. Differential Chromatogram of Sample X-2 After Cleanup (40.7 µg/L)

TABLE 11. TOXAPHENE LEVELS IN INDUSTRIAL WASTE EFFLUENT

Sample ID	Spiking Level (µg/L)	Concentration (µg/L)			
		Pre-Cleanup		Post-Cleanup	
		ECD	TMECD	ECD	TMECD
X-1A		123 112	108 105	119	111
X-1B		126	123	121	106
X-1C	86.3	235	195	194 199	184 182
X-2		43.2	43.2	39.9	40.7
X-3		158	112	147 150	130 127
X-4		35.0 33.4	38.3 37.3	39.0	38.4

TABLE 12. STATISTICAL SUMMARY: PRECISION ESTIMATES OF RECOVERY FOR TOXAPHENE IN WASTE EFFLUENT SAMPLES

Method	Intralaboratory % Relative Standard Deviation	
	Estimate	Approximate 95% Confidence Limit
Pre-Cleanup		
Commercial ECD	6.8	(3.7, 26)
TM ECD	12.7	(7.2, 47)
Post-Cleanup		
Commercial ECD	1.8	(1.0, 6.8)
TM ECD	1.8	(1.0, 6.8)

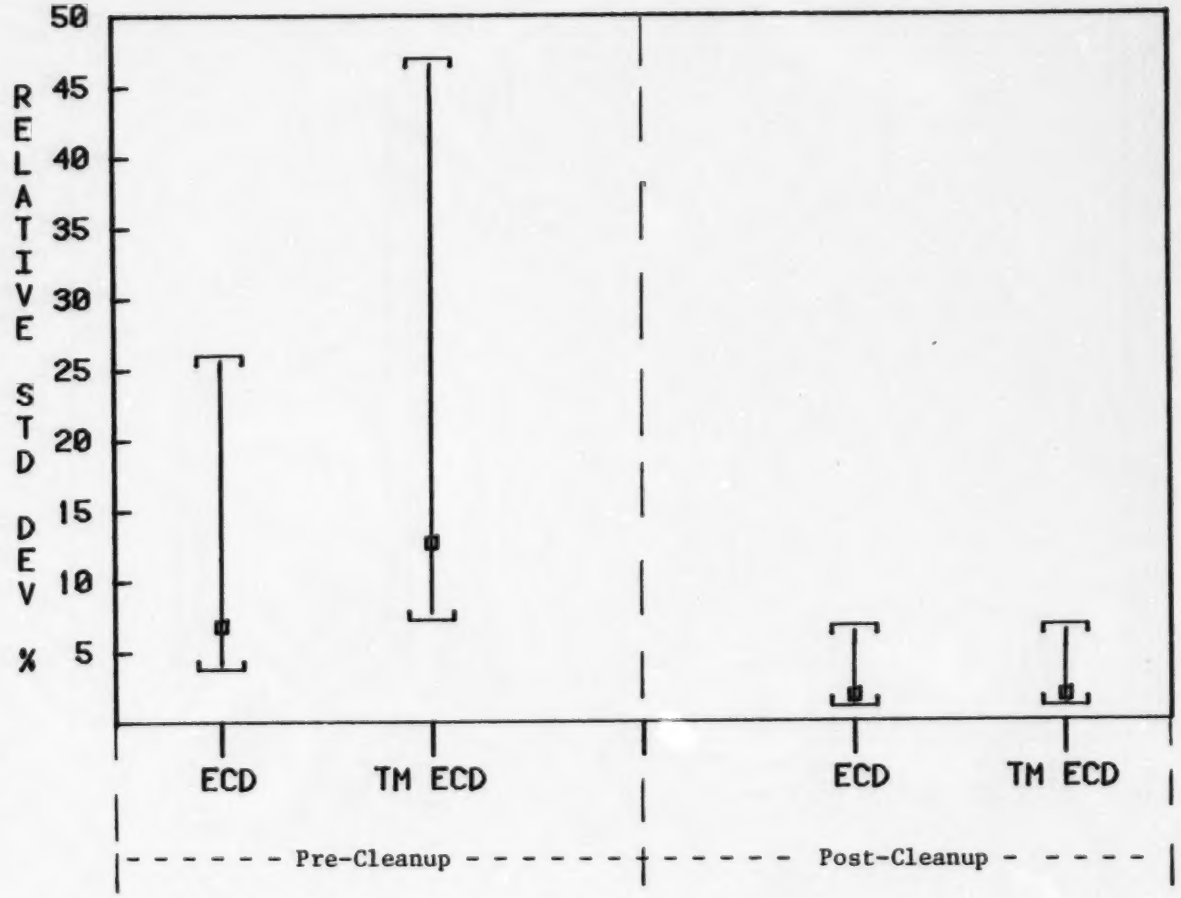

Figure 18. Precision Estimates for Toxaphene Determinations in Waste Effluents (Estimate ⊡ 95% Confidence Interval)

TABLE 13. METHOD RECOVERY CHECK

Parameter	Concentration (µg/L)			
	Pre-Cleanup		Post-Cleanup	
	ECD	TMECD	ECD	TMECD
Average toxaphene conc. (Samples X1-A and X1-B)	122	114	120	108
Toxaphene spiking level (µg/L)	86	86	86	86
Predicted toxaphene concentration (µg/L)	208	200	206	194
Analyzed toxaphene concentration (µg/L)	235	195	196	183
% Toxaphene recovery	113	98	95	94

and Ar/CH_4 carrier gas. An attempt was made to compare the post-reactor response of an equivalent amount of di-n-butyl phthalate to that of the phthalic anhydride.

The phthalic anhydride chromatographic peak tailed so badly, however, that it was impossible to get an accurate comparison. Consequently, it was not possible to conclusively identify the formation of phthalic anhydride as the underlying mechanism for the phthalate ester response characteristics. Nevertheless, it was found that phthalic anhydride was more sensitive than the phthalate ester. The difference between the sensitivities of the anhydride and the ester was approximately the same as the elevated response observed for the ester after passing through the reactor at 850°C. Thus, the formation of phthalic anhydride is a plausible reaction mechanism.

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